IMPROVEMENT IN DURABILITY OF FERROCEMENT THROUGH CORROSION INHIBITORS

SYNOPSIS OF THE THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

IN

CIVIL ENGINEERING

BY

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1. INTRODUCTION

Socio-economic factors have always influenced construction practices. Man has invariably attempted to compose materials that are not only cheap and easy to employ, but also strong and durable. Fibre composites being lightweight, eco-friendly, cost effective and structurally efficient, happen to be an ideal choice for construction industry. Ferrocement is one such composite material which consists of layered wire meshes and rich cement-sand mortar. The uniform distribution and high surface area to volume ratio (specific surface) of the reinforcement results in a good crack arrest mechanism. It has high degree of ductility and energy absorbing capacity and has been increasingly used both in terrestrial and marine environments. However, the durability of ferrocement has always been a point of concern owing to the corrosion susceptibility of the small diameter metallic wire meshes. The corrosion of steel reinforcement leads to matrix fracture, loss of bond between steel and matrix, and reduction in strength and ductility. As a result, safety, serviceability and durability of structural components/structures are reduced. The present study is aimed at preventing the corrosion in the ferrocement composites by using corrosion inhibitors and thereby improving the durability of the composites.

2. LITERATURE REVIEW

Ferrocement has proven itself as an excellent material for low cost housing (Arif *et al.*, 2001; Naaman, 2006) Investigations on the use of pre-cast ferrocement elements in low cost housing have proved the effectiveness of the material system under static conditions. The prefabricated ferrocement elements have also been used successfully in both residential and industrial buildings (Rivas, 1994). Experimental and analytical studies on the flexural behaviour of ferrocement plates have also proved the material worthiness for use in diversified applications (Balaguru, Naaman and Shah, 1977; Arif, Pankaj and Kaushik, 1999; Kaushik *et al.*, 2002; Pankaj, Arif and Kaushik, 2002). Extensive experimental tests conducted on ferrocement under flexural fatigue and impact also suggest that the ferrocement structural system has got great potentials to serve as a low cost alternative under dynamic environment (Arif, Pankaj and Kaushik, 1998). Various research organisations and non government agencies viz. CBRI, SERC, AVBC, HUDCO and some other private sector organisations have also been involved in propagating the technology for effective use of ferrocement units. In addition to promotion of technology and training of construction workers, SERC and HUDCO are also engaged in construction of rehabilitation projects through state agencies.

Success of ferrocement, as with other material depends largely upon its durability. Reinforcement corrosion is one of the most important criterion governing durability of the ferrocement since the diameter of the wire meshes used in ferrocement are much smaller as compared to the conventional reinforced cement concrete. Protection of reinforcement is usually achieved through the use of galvanized wire mesh. It has been found that even the condition of galvanized wire meshes deteriorates under aggressive environment (Masood *et al.*, 2003). It has also been suggested that by making dense mortar with the use of additives such as fly ash, silica fumes and blast furnace slag, corrosion of reinforcement can be checked to some extent (Dotto *et al.*, 2004). Some researchers have reported an improvement by means of an increase in the effective cover (Vickridge, Nakassa and Turner, 1998). These suggested ways have proved to be ineffective with the passage of time, thereby, reducing the strength of the ferrocement components (Torri and Kawamura,

1990; Ramesht, 1995). Studies undertaken on the chemical reactivity of inhibitors by earlier investigators highlight the worthiness of its application (Rosenberg and Gaidis, 1978; Whiting, 1979; Kilareski, 1980; Raman and Labine, 1996; Quraishi and Jamal, 2003). ACI-549R strongly recommends that studies be undertaken to suggest durable and long term anti corrosion techniques to prevent penetration of water and salts that could lead to the corrosion of reinforcing wire mesh (ACI 549R-03, 2003). Very recently, some investigations have been undertaken to study the behaviour of corrosion inhibitors, in protecting reinforcement in concrete. Calcium Nitrite has been suggested as one such corrosion inhibitor. Its effect on hydration of cement as well as its long-term effect have also been reported (Gaidis, 2004; Berke and Hicks, 2004; Sideris and Savva, 2005; Saraswathy and Song, 2007). A number of organic and inorganic corrosion inhibitors and their properties have been explored (Kuban, Raman and Gale, 1995; Quraishi and Rawat, 2002; Nmai, 2004; Quian and Cusson, 2004). The usefulness of migratory corrosion inhibitors in protecting reinforcement in concrete exposed to marine environment has also been studied (Malik *et al.*, 2004). Use of corrosion inhibitors in repair of concrete structures and its electrochemical behaviour has also been investigated (Ngala, Page and Page, 2000; Vaysburd and Emmons, 2004; Trabanelli *et al.*, 2005; Ormellese *et al.*, 2006). Although the worthiness of corrosion inhibitors in reinforced concrete is very well reported, its application methodology, dose and subsequent effects continue to be unexplored for ferrocement. There is a wide scope left to suggest new dimensions and new methodology, which can seize/reduce the corrosion with the passage of time, thereby adding extra life to the structure. No breakthroughs have so far been made for the protection of wire meshes in ferrocement through corrosion inhibitors.

3. OBJECTIVES OF THE STUDY

The present study is aimed at preventing the corrosion in the ferrocement composites by using corrosion inhibitors and thereby improving the durability of the composites. The broad objectives of the present investigation are:

(i). To carryout an extensive survey of literature pertaining to the topic of study in the related area so as to thoroughly and critically review the advancement made till date and to identify and select a few corrosion inhibitors which may be used for effective corrosion control in ferrocement.

(ii). To investigate the problems arising out of the use of these corrosion inhibitors *e.g.* early/delayed setting time, compressive and tensile strength of the matrix and the effect on the pH value of the various systems of exposure.

(iii). To carry out micro-level visual examination of both the un-inhibited and inhibited mortar specimens using scanning electron microscopy (SEM) images in order to study the microstructure of the matrix.

(iv). To undertake detailed investigations on corrosion kinetic parameters using electrochemical tests on these inhibitors.

(v). To study the performance of the corrosion inhibitors for various types of specimens *viz.* mild steel plate, naked welded wire mesh specimen and cement slurry coated welded wire mesh specimen, with varying dose of inhibitors, exposure duration and exposure medium. Further, to study the deterioration of these specimens through naked eye as well as high resolution microscopic observations.

(vi). To find out most appropriate dose and application methodology for the selected inhibitors, by undertaking tests on ferrocement cuboid specimens exposed to normal and simulated aggressive environment and to undertake a comparative assessment of the physical condition of the reinforcement through visual observations.

(vii). To study the flexural behaviour and failure characteristics of inhibited ferrocement plate specimens under potable as well as saline water medium.

(viii). To study the mechanism of corrosion and inhibition and to find optimum specifications regarding the use of corrosion inhibitors, its application methodology and dose.

4. SELECTION OF CORROSION INHIBITORS

The first part of the study was aimed at investigating the effect of four corrosion inhibitors namely calcium nitrite, calcium nitrate, tannic acid and calcium stearate on various parameters controlling the strength and durability of ferrocement. The effect of dose of corrosion inhibitors on setting time of cement; compressive and tensile strength of cement sand mortar was determined. The doses of the inhibitors were varied as 1%, 3% and 5% by the weight of the cement. The compressive and tensile strength of the control and inhibited mortar was observed at 3, 7, 14, 28 and 90 *days*. It has been observed that most of these inhibitors acted as an accelerator to the initial and final setting of cement, though the rate of acceleration was different in each case. However, it is interesting to note that at higher doses, some of the inhibitors (5% calcium nitrite and tannic acid) behaved as retarders. The values of the initial and final setting time are within the recommended limits of the relevant codes of practice. An increase in compressive and tensile strength has been observed with age for the control, saline and most of the mortar mixes having different percentages of the corrosion inhibitors. For some inhibitors, the early gain in strength was much lower than the control specimen especially for the inhibited specimens containing 3% and 5% dose of tannic acid and calcium stearate. Slow gain in strength at early age in some of the combinations can be attributed to the slow down of the reaction of C_3S by the addition of these chemicals in high concentration. A significant increase in strength after 28 *days* has been observed for calcium nitrate due to the fact that the C_3S reaction gains momentum after 28 *days*. These chemicals might be acting as a catalyst to the C_2S reaction too, which also contributes to the gain in delayed strength.

Tests were also conducted on solutions to observe pH values for different doses of corrosion inhibitors. With calcium nitrite inhibitor, the pH value increases whereas for calcium nitrate, tannic acid and calcium stearate there is a slight reduction in pH value. When these inhibitors are used in cement slurry solution, the pH value is generally found to above 12.

The SEM images for control specimens in potable water reveal a normal hydrated structure such as calcium silicate hydrate (*CSH*) gel, scattered crystallized calcium hydroxide and unfilled pores. However, for the control specimen in saline water, pores appear to be filled by sodium chloride crystals whereas for the inhibited specimens with the crystals of inhibitors. The strength variation is on account of enhanced packing and chemical reactions of the inhibitor with C_3S, C_2S and C_3A.

The electrochemical Tafel extrapolation and AC-impedance technique were applied to study the corrosion as well as electrochemical activity at the mild steel interface with and without the protective treatments for 1% and 5% dose of inhibitors. These tests indicate a better

performance for calcium nitrite inhibitor as compared to other three inhibitors. The calcium nitrate did not perform well. In some cases calcium stearate has shown better results whereas in some other conditions tannic acid performed well. The calcium nitrite and tannic acid inhibitors were finally chosen as the best inorganic and organic inhibitors respectively for further studies.

5. TESTS ON MILD STEEL PLATE, NAKED AND SLURRY COATED WIRE MESH

Gravimetric weight loss method was used for the assessment of extent of corrosion in three types of specimen *viz.* mild steel plate, welded steel wire mesh and cement slurry coated wire mesh specimens, to evaluate the effectiveness of calcium nitrite and tannic acid inhibitors. The weight loss, efficiency of corrosion inhibitors, corrosion rate and penetration rate were the main parameters under investigation. A total of six exposure mediums namely potable water (normal tap water), potable water with calcium nitrite (Type–I) and Tannic acid (Type–II) inhibitors and artificial saline water (distilled water mixed with 4% *NaCl*), saline water with Type–I and Type–II inhibitors were undertaken for the present investigation. The exposure time was 30, 90, 180 and 360 *days* at room temperature. The doses of Type–I and Type–II inhibitors were kept as 1%, 3% and 5%. For each exposure medium, the specimens were used in triplicate. Both the quantitative and the qualitative observations were made.

All the three types of specimens undergo higher corrosion when exposed to saline water medium as compared to their counterparts exposed to potable water medium for all of the exposure durations considered. For the mild steel plate specimens and naked welded steel wire mesh specimens, only 1% dose of the calcium nitrite is sufficient in controlling the corrosion in potable water medium. However, in saline water medium 1% dose is effective only up to short duration of exposure whereas, for longer durations a dose of 3% was found to be sufficient. The reason behind 1% dose of calcium nitrite being not so effective appears to be the higher chloride to nitrite ratio. For longer durations in saline water medium calcium nitrite dose of just above 3% is found to be sufficient. However, at 5% dose the specimen was almost in fully passive state. Tannic acid inhibitor has not been found to be very effective in controlling the corrosion, owing to the dissolution of protective coating in the aqueous solution.

For the cement slurry coated welded steel wire mesh specimens, the calcium nitrite dose of 3% was found to be sufficient in checking the corrosion both in potable; and saline water medium. For the tannic acid sufficient protection has been observed for all the doses for all exposure durations. The protection of the tannic acid film by cement slurry coat helps in corrosion prevention. The corrosion inhibition efficiency, corrosion rate and corrosion penetration values for these inhibitors also substantiate the above findings.

High magnification microscopic images of the specimens were captured at 400X, wherein corrosion free and spotless surface can be seen, thereby, making it explicitly clear that the corrosion inhibitors play a key role in mitigating/controlling corrosion in both potable and saline water exposure medium.

6. TESTS ON FERROCEMENT CUBOIDS

Ferrocement cuboid specimens of overall size 38×38×24 *mm* were cast using three layers of wire meshes and exposed to simulated environment for a period of 360 *days* to monitor the effectiveness of calcium nitrite and tannic acid inhibitors. The dose of the inhibitors was kept as 1%, 3% and 5%. Different application methodologies were used for these inhibitors. The exposure duration was taken as 30, 90, 180 and 360 *days* for both potable and saline water exposure medium. The corrosion inhibition efficiency, corrosion rate and penetration rate were investigated. Apart from quantitative study using gravimetric weight loss method, qualitative observations were also made. The calcium nitrite was once mixed directly into the cement sand mix by weight of the cement. In the second case it was mixed in cement slurry by weight of cement and the resulting paste was used to form a coating of this inhibited cement slurry over the surface of the wire mesh. Tannic acid was also used in two ways. In the first case, coating of tannic acid was formed as a thin film over the wire mesh. In the second mode of application of tannic acid, a protective coating of plain cement slurry was applied over the film of tannic acid. The specimens were exposed to alternate wetting and drying cycles of 5 *days* wet and 5 *days* dry duration under both potable and saline water medium for 360 *days*.

For ferrocement cuboid specimens, at 3% and 5% dose of calcium nitrite in both the situations *i.e.* when it has been mixed with the mortar (NW I) or when applied in the form of inhibited cement slurry (NW SC I), a perfect passive state has been achieved even after 360 *days* of exposure. Visual inspection substantiates these observations. Even for 1% dose applied in the form of the inhibited cement slurry (NW SC I-1), satisfactory inhibition has been achieved. For the cuboid specimens in saline water exposure medium, 5% dose of calcium nitrite gives the absolute passive state for both the application methodologies (SW I and SW SC I), although even at 3% dose, quite high inhibition has been obtained. Within the two modes of application of calcium nitrite, the one, where the inhibitor is applied in the form of inhibited cement slurry (NW SC I and SW SC I), appears to perform better since the inhibitor is present in high concentration and in close contact with the reinforcement. It neither affects the setting time of the cement nor influences the chemical reactions which take place during the process of hydration. Another advantage is the cost effectiveness of this application technique.

For the tannic acid inhibited cuboid specimens, best results have been obtained for the specimens where the tannic acid film over the wire mesh was protected by the cement slurry coating (NW SC II and SW SC II). Effect of increase in the dose of tannic acid seems to be very marginal. In potable water exposure medium, the level of inhibition exhibited by all the doses is extremely high. In saline water medium, however, 3 and 5% doses have shown high inhibition. The reason behind the ineffectiveness of the tannic acid in the form of film without the protection of the cement slurry coating at lower dose is its dissolution in the presence of diluents. Visual examination of the specimens of this category also confirms the above findings. As the weight loss in the inner layer of wire mesh is only marginally less than the outer layer of the wire mesh, it can be fairly concluded that even a higher mortar thickness available for the inner wire meshes, provides only a little relief from corrosion. It is, therefore, pertinent here to plan out strategies for the corrosion protection of both outer and inner wire mesh layers. Very high durability factor has been obtained for most of the calcium nitrite inhibited specimens, which clearly indicates its effectiveness in enhancing the life of the reinforcement used in the form of meshes. Even for the tannic acid, except for a few of the combinations, reasonably high durability factor has been observed.

7. FLEXURAL TESTS ON FERROCEMENT PLATES

Experimental investigations were finally undertaken on scaled ferrocement plate specimens of size 370×150×24 *mm* prepared in three layers of wire meshes, using calcium nitrite and tannic acid inhibitors to establish their suitability for controlling and mitigating the corrosion ingress with main focus on the load-deflection behaviour vis-à-vis failure characteristics of the specimens. These plate specimens were exposed to simulated environment for a period of 360 *days*. Same combinations of inhibitor dose and application methodology, as used for ferrocement cuboid specimens, were used. The dose of the inhibitors was kept as 1%, 3% and 5%. Both potable and saline water exposure medium were used and the specimens were exposed to alternate 5 *days* wetting and 5 *days* drying cycles. To get clear crack patterns, air dried specimens were white washed before the test. These specimens were tested under flexure in INSTRON universal testing machine. A pronounced corrosion activity, resulting in a considerable loss in flexural strength, is observed in un-inhibited ferrocement plate specimens exposed to potable water medium (PNW) as well as saline water medium (PSW). The failure is mainly on account of de-bonding of wire mesh layers with the mortar layers. A far more severe corrosion is observed in PSW series of specimens. The corrosion of the wire meshes and the subsequent loss of bond between the mortar and the wire mesh reinforcement, are primarily the main reasons behind the low load carrying capacity of these specimens. As the loads are increased, both the numbers of cracks as well as the crack width were found to increase. The failure of the PSW series of specimens, takes place at low strain values and thus rendering it to behave like a brittle system. The cracks on the bottom surface for PNW and PSW series of specimens further validate these observations.

For plate specimens exposed to potable water medium, best results are obtained for calcium nitrite inhibitor at all the doses. For both the two application methodologies, *i.e.* when it is used in mix (PNW I Series) and when it is used in slurry coated form (PNW SC I Series), an increase in the first crack load and the ultimate load has been observed. Highest increase in flexural strength was obtained for the specimen inhibited with 5% calcium nitrite mixed with mortar mainly because of the protection provided by the calcium nitrite to the wire mesh reinforcement, thereby, providing a perfect bond between mortar and the wire meshes. Also, the mortar strength increases due to higher percentage of the calcium nitrite, hence improving the composite strength as a whole. The specimens with cement slurry protection over tannic acid coating (PNW SC II) have shown appreciable increase especially at 3% and 5% inhibitor dose. However, in the specimens where no such protection (PNW II) has been provided to the tannic acid coating, only a marginal increase in the strength is observed. The specimen failed through de-lamination of the mortar layers, indicating loss of bond between the mortar and the reinforcement due to corrosion ingress.

In saline water medium the ferrocement plate specimens inhibited with the calcium nitrite, show a higher flexural strength for 3% and 5% dose of inhibitor in both the two application schemes, whether calcium nitrite was mixed in mortar (PSW I) or used in slurry coated form (PSW SC I). Higher Cl^-/NO_2^- ratio is the reason behind 1% dose of calcium nitrite not being so effective in mitigating corrosion. The failure is triggered by de-bonding of wire mesh layers with the mortar layers. An excessive corrosion activity appears to be the reason behind this. For the tannic acid inhibited specimens (PSW II) exposed to saline water medium, inhibition efficiency similar to the specimens inhibited with calcium nitrite is

observed only at 5% dose. The reason behind the effectiveness of inhibitors appears to be a thick coating of the tannic acid that remains effective even after it gets dissolved with the passage of time. However, at lower doses, a marginal increase in the value of flexural strength is found. For specimens inhibited with tannic acid film protected with the cement slurry (PSW SC II), the flexural strength almost 100% higher than the control specimen has been observed. A very good bond between the wire mesh reinforcement and the mortar results in a perfect composite action leading to ductile failure.

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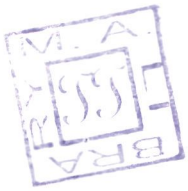

"When we build, let us think that we build for ever. Let it not be for the present delight or for the present use alone. Let it be such a work as our descendants will thank us for..."

John Ruskin (1819-1900)

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled ***Improvement in Durability of Ferrocement through Corrosion Inhibitors*** in fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Civil Engineering of the University, is an authentic record of my own work carried out under the supervision of Dr. Mohammed Arif and Prof. M. A. Quraishi.

The matter presented in this thesis has not been submitted by me for the award of another degree of this or any other University.

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Signature of Supervisor(s) Signature of Chairman Signature of External Examiner

ABSTRACT

Ferrocement is a composite material which consists of layered wire meshes and rich cement-sand mortar. The uniform distribution and high surface area to volume ratio (specific surface) of the reinforcement results in a good crack arrest mechanism. It has high degree of ductility and energy absorbing capacity and has been increasingly used both in terrestrial and marine environments. However, the durability of ferrocement has always been a point of concern owing to the corrosion susceptibility of the small diameter metallic wire meshes. The corrosion of steel reinforcement leads to matrix fracture, loss of bond between steel and matrix, and reduction in strength and ductility. The corrosion protection of reinforcement in ferrocement is usually achieved through the use of galvanized wire mesh, increased cover or with the use of dense mortar achieved by additives such as fly ash, silica fumes and blast furnace slag. With time, these measures have proved to be ineffective, thereby reducing the strength of the ferrocement components. ACI-549R strongly recommends that studies be undertaken to suggest durable and long term anti-corrosion techniques to prevent penetration of water and salts that could lead to the corrosion of reinforcing wire mesh. Some recent studies clearly establish the effectiveness of corrosion inhibitors in controlling/delaying onset of corrosion. The present study is aimed at preventing the corrosion in the ferrocement composites by using corrosion inhibitors and thereby improving the durability of the composites. The broad objectives of the present investigation are:

(i). To carryout an extensive survey of literature pertaining to the topic of study in the related area so as to thoroughly and critically review the advancement made till date and to identify and select a few corrosion inhibitors which may be used for effective corrosion control in ferrocement.

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(vii). To study the flexural behaviour and failure characteristics of inhibited ferrocement plate specimens under potable as well as saline water medium.

(viii). To study the mechanism of corrosion and inhibition and to find optimum specifications regarding the use of corrosion inhibitors, its application methodology and dose.

The first part of the study was aimed at investigating the effect of four corrosion inhibitors namely calcium nitrite, calcium nitrate, tannic acid and calcium stearate on various parameters controlling the strength and durability of ferrocement. The effect of dose of corrosion inhibitors on setting time of cement; compressive and tensile strength of cement sand mortar was observed. The doses of the inhibitors were varied as 1%, 3% and 5% by the weight of the cement. The compressive and tensile strength of the control and inhibited mortar were determined at 3, 7, 14, 28 and 90 *days*. It has been observed that most of these inhibitors acted as an accelerator to the initial and final setting, though the rate of acceleration was different in each case. However, it is interesting to note that at higher doses, some of the inhibitors (5% calcium nitrite and tannic acid) behaved as retarders. The values of the initial and final setting time are within the recommended limits of the relevant codes of practice. An increase in compressive and tensile strength has been observed with age for the control, saline and most of the mortar mixes having different percentages of the corrosion inhibitors. For some inhibitors, the early gain in strength was much lower than the control specimen especially for the inhibited specimens containing 3% and 5% dose of tannic acid and calcium stearate. Slow gain in strength at early age in some of the combinations can be attributed to the slow down of the reaction

of C_3S by the addition of these chemicals in high concentration. A significant increase in strength after 28 *days* has been observed for calcium nitrate due to the fact that the C_3S reaction gains momentum after 28 *days*. These chemicals might be acting as a catalyst to the C_2S reaction too, which also contributes to the gain in delayed strength.

Tests were also conducted on solutions to observe pH values for different doses of corrosion inhibitors. With calcium nitrite inhibitor, the pH value increases whereas for calcium nitrate, tannic acid and calcium stearate there is a slight reduction in pH value. When these inhibitors are used in cement slurry solution, the pH value is generally found to above 12.

The SEM images for control specimens in potable water reveal a normal hydrated structure such as calcium silicate hydrate (*CSH*) gel, scattered crystallized calcium hydroxide and unfilled pores. However, for the control specimen in saline water, pores appear to be filled by sodium chloride crystals whereas for the inhibited specimens with the crystals of inhibitors. The strength variation is on account of enhanced packing and chemical reactions of the inhibitor with C_3S, C_2S and C_3A.

The electrochemical Tafel extrapolation and AC-impedance technique were applied to study the corrosion as well as electrochemical activity at the mild steel interface with and without the protective treatments for 1% and 5% dose of inhibitors. These tests indicate a better performance for calcium nitrite inhibitor as compared to other three inhibitors. The calcium nitrate did not perform well. In some cases calcium stearate has shown better results whereas at a dose of 1%, tannic acid performed well. The calcium nitrite and tannic acid inhibitors were finally chosen as the best inorganic and organic inhibitors respectively for further studies.

Gravimetric weight loss method was used for the assessment of extent of corrosion in three types of specimen *viz.* mild steel plate, naked welded steel wire mesh and the cement slurry coated welded steel wire mesh specimens, to evaluate the effectiveness of calcium nitrite and tannic acid inhibitors. The weight loss, efficiency of corrosion inhibitors, corrosion rate and penetration rate were the main parameters under investigation. A total of six exposure mediums namely potable water (normal tap water),

potable water with calcium nitrite (Type–I) and Tannic acid (Type–II) inhibitors and artificial saline water (distilled water mixed with 4% *NaCl*), saline water with Type–I and Type–II inhibitors were undertaken for the present investigation. The exposure time was 30, 90, 180 and 360 *days* at room temperature. The doses of Type–I and Type–II inhibitors were kept as 1%, 3% and 5%. For each exposure medium, the specimens were used in triplicate. Both the quantitative and the qualitative observations were made.

All the three types of specimens undergo higher corrosion when exposed to saline water medium as compared to their counterparts exposed to potable water medium for all of the exposure durations considered. For the mild steel plate specimens and naked welded steel wire mesh specimens, only 1% dose of the calcium nitrite is sufficient in controlling the corrosion in potable water medium. However, in saline water medium 1% dose is effective only up to short duration of exposure whereas, for longer durations a dose of 3% was found to be sufficient. The reason behind 1% dose of calcium nitrite being not so effective appears to be the higher chloride to nitrite ratio. For longer durations in saline water medium calcium nitrite dose of just above 3% is found to be sufficient. However, at 5% dose the specimen was almost in fully passive state. Tannic acid inhibitor has not been found to be very effective in controlling the corrosion, owing to the dissolution of protective coating in the aqueous solution.

For the cement slurry coated welded steel wire mesh specimens, the calcium nitrite dose of 3% was found to be sufficient in checking the corrosion both in potable; and saline water medium. For the tannic acid sufficient protection has been observed for all the doses for all exposure durations. The protection of the tannic acid film by cement slurry coat helps in corrosion prevention. The corrosion inhibition efficiency, corrosion rate and corrosion penetration values for these inhibitors also substantiate the above findings.

High magnification microscopic images of the specimens were captured at 400X wherein corrosion free and spotless surface can be seen, thereby, making it explicitly clear that the corrosion inhibitors play a key role in mitigating/controlling corrosion in both potable and saline water exposure medium.

Ferrocement cuboid specimens of overall size 38×38×24 *mm* were cast using three layers of wire meshes and exposed to simulated environment for a period of 360 *days* to monitor

the effectiveness of calcium nitrite and tannic acid inhibitors. The dose of the inhibitors was kept as 1%, 3% and 5%. Different application methodologies were used for these inhibitors. The exposure duration was taken as 30, 90,180 and 360 *days* for both potable and saline water exposure medium. The corrosion inhibition efficiency, corrosion rate and penetration rate were investigated. Apart from quantitative study using gravimetric weight loss method, qualitative observations were also made. The calcium nitrite was once mixed directly into the cement sand mix by weight of the cement. In the second case it was mixed in cement slurry by weight of cement and the resulting paste was used to form a coating of this inhibited cement slurry over the surface of the wire mesh. Tannic acid was also used in two ways. In the first case, coating of tannic acid was formed as a thin film over the wire mesh. In the second mode of application of tannic acid, a protective coating of plain cement slurry was applied over the film of tannic acid. The specimens were exposed to alternate wetting and drying cycles of 5 *days* wet and 5 *days* dry duration under both potable and saline water for 360 *days*.

For ferrocement cuboid specimens, at 3% and 5% dose of calcium nitrite in both the situations *i.e.* when it has been mixed with the mortar (NW I) or when applied in the form of inhibited cement slurry (NW SC I), a perfect passive state has been achieved even after 360 *days* of exposure. Visual inspection substantiates these observations. Even for 1% dose applied in the form of the inhibited cement slurry (NW SC I-1), satisfactory inhibition has been achieved. For the cuboid specimens in saline water exposure medium, 5% dose of calcium nitrite gives the absolute passive state for both the application methodologies (SW I and SW SC I), although even at 3% dose, quite high inhibition has been obtained. Within the two modes of application of calcium nitrite, the one, where the inhibitor is applied in the form of inhibited cement slurry (NW SC I and SW SC I), appears to perform better since the inhibitor is present in high concentration and in close contact with the reinforcement. It neither affects the setting time of the cement nor influences the chemical reactions which take place during the process of hydration. Another advantage is the cost effectiveness of this application technique.

For the tannic acid inhibited cuboid specimens, best results have been obtained for the specimens where the tannic acid film over the wire mesh was protected by the cement slurry coating (NW SC II and SW SC II). Effect of increase in the dose of tannic acid seems to be very marginal. In potable water exposure medium, the level of inhibition

exhibited by all the doses is extremely high. In saline water medium, however, 3 and 5% doses have shown high inhibition. The reason behind the ineffectiveness of the tannic acid in the form of film without the protection of the cement slurry coating at lower dose is its dissolution in the presence of diluents. Visual examination of the specimens of this category also confirms the above findings. As the weight loss in the inner layer of wire mesh is only marginally less than the outer layer of the wire mesh, it can be fairly concluded that even a higher mortar thickness available for the inner wire meshes, provides only a little relief from corrosion susceptibility. It is, therefore, pertinent here to plan out strategies for the corrosion protection of both outer and inner wire mesh layers. Very high durability factor has been obtained for most of the calcium nitrite inhibited specimens, which clearly indicates its effectiveness in enhancing the life of the reinforcement used in the form of meshes. Even for the tannic acid, except for a few of the combinations, reasonably high durability factor has been observed.

Experimental investigations were finally undertaken on scaled ferrocement plate specimens of size 370×150×24 *mm* prepared in three layers of wire meshes, using calcium nitrite and tannic acid inhibitors with main focus on their load-deflection behaviour vis-à-vis failure characteristics. These specimens were exposed to simulated environment for a period of 360 *days*. Same combinations of inhibitor dose and application methodology, as used for ferrocement cuboid specimens, were used. The specimens were exposed to alternate 5 *days* wetting and 5 *days* drying cycles in potable and saline water medium. To get clear crack patterns, air dried specimens were white washed before the test. These specimens were tested under flexure in INSTRON universal testing machine. A pronounced corrosion activity, resulting in a considerable loss in flexural strength, is observed in un-inhibited ferrocement plate specimens exposed to potable water medium (PNW) as well as saline water medium (PSW). The failure is mainly on account of de-bonding of wire mesh layers with the mortar layers. A far more severe corrosion is observed in PSW series of specimens. The corrosion of the wire meshes and the subsequent loss of bond between the mortar and the wire mesh reinforcement, results in a low load carrying capacity of these specimens. As the loads are increased, both the numbers of cracks as well as the crack width increase. The failure of the PSW series of specimens, takes place at low strain values and thus rendering it to behave like a brittle system. The cracks on the bottom surface for PNW and PSW series of specimens further validate these observations.

For plate specimens exposed to potable water medium, best results are obtained for calcium nitrite inhibitor at all the doses. For both the two application methodologies, *i.e.* when it is used in mix (PNW I Series), and when it is used in slurry coated form (PNW SC I Series), an increase in the first crack load and the ultimate load has been observed. Highest increase in flexural strength was obtained for the specimen inhibited with 5% calcium nitrite, mixed with mortar mainly because of the protection provided by the calcium nitrite to the wire mesh reinforcement thereby providing a perfect bond between mortar and the wire meshes. Also, the mortar strength increases due to higher percentage of the calcium nitrite, hence improving the composite strength as a whole. The specimens with cement slurry protection over tannic acid coating (PNW SC II) have shown appreciable increase especially at 3 and 5% inhibitor dose. However, in the specimens with no protection to the tannic acid coating (PNW II), only a marginal increase in the strength is observed. The specimen failed through de-lamination of the mortar layers, indicating loss of bond between the mortar and the reinforcement.

In saline water medium, the ferrocement plate specimens inhibited with the calcium nitrite show a higher flexural strength for 3% and 5% dose of inhibitor, when calcium nitrite was mixed in mortar (PSW I) or used in slurry coated form (PSW SC I). Higher Cl^-/NO_2^- ratio is the reason behind 1% dose of calcium nitrite not being so effective in mitigating corrosion. The failure is triggered by de-bonding of wire mesh layers with the mortar layers due to excessive corrosion activity. For the tannic acid inhibited specimens (PSW II) exposed to saline water medium, inhibition efficiency similar to the specimens inhibited with calcium nitrite is observed only at 5% dose owing to a thick coating of the tannic acid that remains effective even after its dissolution with time. At lower doses, a marginal increase in flexural strength is noticed. For specimens with tannic acid film protected with the cement slurry (PSW SC II), a two fold increase in flexural strength has been observed as compared to control specimen. A perfect composite action on account of a very good bond between mortar and mesh leads to ductile failure.

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SABIH AKHTAR

CONTENTS

LIST OF NOTATIONS

Notations	Description
$\|z\|$	Cell impedance
a	Inter electrode distance
A	Surface area of the specimen
b_a	Anodic Tafel slope
b_c	Cathodic Tafel slope
C_{dl}	Double layer capacitance
D	Density of the specimen
E_c	Composite modulus
E_{corr}	Corrosion potential
E_{cr}	Composite modulus in cracked range
E_t	Composite modulus in transverse direction
f	Frequency
f_y	Stress at yield
I	Charpy impact strength
I_{corr}	Corrosion current density
N_f	Fatigue life
R	Measured resistance
R_{ct}	Charge transfer resistance
R_p	Polarization resistance
R_s	Resistance of medium
S_r	Stress range in extreme layer
S_R	Surface steel ratio
T	Exposure time
V_f	Volume fraction of fibre
W	Weight loss of specimen
W_f	Weight of the specimen after exposure
W_i	Weight of the specimen before exposure
ΔE	Potential difference
ΔI	Small DC current
ε	Strain

ε_{cu}	Compressive strain in composite at ultimate condition
ε_{cy}	Compressive strain in composite at first crack condition
ε_{tu}	Tensile strength in composite at ultimate condition
ε_{ty}	Tensile strength in composite at yielding condition
ρ	Resistivity of concrete
σ	Stress
σ_{cr}	Composite stress at first crack in tension
σ_{cu}	Ultimate strength of composite in axial tension
σ_{cy}	Composite stress in compression at yielding
σ_{ty}	Composite stress at yielding in tension

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Introduction

1.1 FERROCEMENT

Socio-economic factors have always influenced construction practices. Man has invariably attempted to compose materials that are not only cheap and easy to employ, but also strong and durable. Ferrocement is one such composite material in which rich cement-sand mortar (or micro-concrete) is reinforced with layers of continuous and small diameter steel wire meshes. The basic principle in its formulation is that concrete can undergo large strains in the neighbourhood of reinforcement and the magnitude of strains depends on the distribution and subdivision of meshes in concrete. The uniform distribution and high surface area to volume ratio (specific surface) of the reinforcement results in a good crack arrest mechanism.

Ferrocement Model Code (2001) defines ferrocement as a type of reinforced concrete commonly constructed of hydraulic cement mortar reinforced with closely spaced layers of relatively small wire diameter mesh. The mesh may be made of metallic or other suitable materials. The fineness of the mortar matrix and its composition should be compatible with the opening and tightness of the reinforcing system it is meant to encapsulate. The matrix may contain discontinuous fibers (Ferrocement Model Code 10-01, 2001).

Ferrocement is used in thin walled structures where strength and rigidity are developed through form or shape. It can be tailored with directional strength properties and has the distinct advantage of being moldable and of one piece construction. Other major advantages are its low cost and non-flammability. The confidence in the material has been building up with time resulting in its wider applications. The application areas of ferrocement are both terrestrial and marine. It has been used in housing (particularly roofing elements), water tanks, pipes, water boats, barges, vessels, reservoirs, swimming pools, farming works, silos and warehouses (Paul and Pama, 1978; Shah and Balaguru, 1984; Kaushik, 1994).

The basic constituent materials required for ferrocement are cement, sand, water and wire meshes. The cement should normally be of ordinary Portland type. It should conform to specifications of IS: 269, 8112 or ASTM Standard C-150 and C-595. The sand should conform to the specifications of IS: 383-1970 or ASTM Standard C-33; C-227 and C-330. The water should be free from impurities. Ordinary potable water, having pH $\geq$ 7, should be used in the mortar. The cement-sand ratio for the mortar varies from 1:1.5 to 1:2.5 and water-cement ratio, from 0.35 to 0.50 by weight. Wire meshes of different types, such as hexagonal (chicken wire mesh), woven, welded, expanded and Watson meshes, have been used. Most common of these are woven and welded wire meshes conforming to ASTM Standards A-496-97a and A-497-99e1. The principal requirement is that they should be easy to handle and flexible enough to be bent around corners, if necessary. The wire meshes may be galvanized or ungalvanized. The wire meshes are generally made up of 0.5 to 1.5 *mm* diameter wires and spaced 5 to 25 *mm* apart. The construction of ferrocement can be divided into four phases *viz.* placement of wire mesh in a proper position, mortar mixing, mortar application and curing with the objective to thoroughly encapsulate a layered mesh system with a micro-concrete matrix (Ferrocement Model Code 10-01, 2001). This is achieved to varying degrees, depending on the particular application, by the use of four principal application procedures: the skeletal armature, closed mould system, integral mould system and open mould system (ACI 549 1R-88, 1988 and 1R-1993). Within these four generic ferrocement moulding systems, mortar may be applied by a variety of production techniques, including direct plastering and shotcreting. The minimum cover to the outermost layer is kept around 2 to 5 *mm*.

Tests on the ferrocement hardened composites include load-deflection response, tensile stress-strain response, compressive strength and modulus, shear resistance, punching shear strength, impact resistance, freeze-thaw and durability tests (Ferrocement Model Code 10-01, 2001).

1.2 HISTORICAL DEVELOPMENT

The history of ferrocement dates back to its first invention by Joseph Louis Lambot in 1849 (Cassie, 1967). Lambot took out French and Belgian patents on what he called 'Ferciment'. One of his boats is on display in a museum in Brignoles. In early 1940's, a noted Italian engineer-architect, Pier Luigi Nervi resurrected the original idea of Lambot when he observed that reinforcing concrete with layers of wire mesh produced a material which possesses the mechanical characteristics of an equivalent homogeneous material and shows greater resistance to impact. He went on to design and construct several roofs which still remain rational and aesthetic models in structural design (Nervi, 1956).

The ferrocement could gain wide acceptance only in early 1960's despite the fact that it was an adequate and economic building material. Significant interest by amateur boat builders in ferrocement and its applications grew. Notable ferrocement applications include de Menil Museum, Houston, Texas, U.S.A. in 1984 designed by the Italian architect Renzo Piano where ferrocement has been used both as a structural and architectural material and manufactured with stringent specifications; Large Shaking Table Facility at the State University of New York at Buffalo in 1986 (Reinhorn and Prawel, 1986); Sewer Pipeline Renovation Systems in U.K. in 1989 (Singh *et al.*, 1989); and more recently Schlumberger Research Laboratory, Cambridge, which also bagged a Commendation in Building Category in U.K. in 1993.

Increased scientific approach to studying and predicting ferrocement properties started in the late 1960's and was encouraged by a panel of the US National Academy of Sciences in 1973. This led to the formation of the American Concrete Institute's Committee on Ferrocement, in 1975, and shortly thereafter, in 1976, the establishment of the International Ferrocement Information Center (IFIC) in Bangkok, Thailand. Publication of the Journal of Ferrocement was then consolidated at IFIC.

A RILEM scientific committee on ferrocement was later formed in 1979. Progress accelerated during the 1980's through fundamental research, publications, symposia, short courses and applications. The International Ferrocement Society (IFS) was founded in 1991 with the objective to foster development, disseminate knowledge, and encourage practical applications of ferrocement. The most urgent need of this new professional society was to develop a building code for ferrocement. The first Ferrocement Model Code was published in 2001 essentially setting the stage for guided expansion, imagineering and developments (Naaman, 2006).

Since then, there has been an increased activity with ferrocement construction throughout the world particularly in Canada, U.S.A., Australia, New Zealand, U.K., Mexico, erstwhile Soviet Union, Poland, Cuba, Hungary, China, Thailand, India, Indonesia and Israel.

1.3 OBJECTIVES OF THE STUDY

Success of ferrocement, as with other materials, depends largely upon its durability. Reinforcement corrosion is one of the most important criteria governing durability of the ferrocement since the diameter of the wire meshes used in ferrocement are much smaller as compared to the conventional reinforced cement concrete. There is an urgent need to suggest the way, which can seize/reduce the corrosion, with the passage of time, thereby adding prolonged life to the structure and hence increase its acceptability.

The objective of this study is to improve the corrosion resistance of the metallic wire meshes used in ferrocement by using corrosion inhibitors and thereby providing a solution technique to address the issues concerning the durability of the fibre reinforced composites. It is important to mention that the service life is a critical issue that governs the acceptability of all fibre reinforced composite materials in real life problems.

A multi-stage scheme of investigation was undertaken. Initially it was aimed at selecting corrosion inhibitors based on some electrochemical tests, tests on physical properties of cement, determination of pH of solutions and one month weight loss studies.

After selecting the corrosion inhibitors, long term weight loss study under direct exposure condition in different environment was carried out. In the next stage of study, the effectiveness of the corrosion inhibitors in controlling/delaying the corrosion initiation, was monitored by exposing cementitious cuboids having wire meshes embedded inside in three layers. Surface observation and weight loss study were carried out over a period of one year. Lastly, ferrocement plates were exposed to similar types of environment as that of the cuboids; and flexural strength and failure behaviour were observed.

A total of four corrosion inhibitors were used in the present study. The level of efficiency exhibited by calcium nitrite inhibitor under all types of exposure conditions clearly indicates its effectiveness in delaying/reducing the corrosion in mild steel plates and steel wire meshes. Tannic acid also appears to be a reasonably good corrosion inhibitor and can be used as a fair alternative for protecting metallic wire meshes from corrosion.

1.4 THESIS ORGANISATION

A brief layout of the thesis following this chapter is as under:

The concept, importance, application, complexities and historical background of the problem are highlighted in Chapter-1.

In Chapter-2, a review of investigations carried out on the mechanical behaviour of ferrocement with a major focus on durability and behaviour under aggressive environment has been undertaken. In addition to this, a detailed review of investigations aimed at corrosion control in reinforced concrete composites through chemical corrosion inhibitors has also been attempted.

Chapter-3 takes a theoretical overview of the reinforcement corrosion mechanism and control. The factors affecting reinforcement corrosion and matrix deterioration as well as their monitoring methods have been discussed. Various corrosion protection methods have also been explained.

Results of setting time of cement; compressive and tensile strength of cement sand mortar, effect of corrosion inhibitors on pH of medium, scanning electron microscope (SEM) investigations and electrochemical tests have been reported in Chapter-4.

Chapter-5 deals with the gravimetric weight loss study conducted on naked mild steel plate, naked welded steel wire mesh and slurry coated welded steel wire mesh under various exposure conditions over a period of one year. Visual examination using high resolution microscope has also been included.

Layer wise weight loss study and visual examination conducted on ferrocement cuboids with various combinations of inhibitors dose and exposure conditions have been presented in the Chapter-6.

In Chapter-7, the results obtained from the flexural tests conducted on ferrocement plates have been reported.

The conclusions and scope for further study have been presented in Chapter-8.

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Review of Literature

2.1 GENERAL

Fibre composites are nowadays becoming a popular choice for construction industry due to its excellent performance and ease of construction. These are usually lightweight, eco-friendly; cost effective and structurally efficient material systems especially the ones which can be tailored to perform the desired functions. The variety of these materials includes ferrocement, steel fibre composites, SIFCON and polymer composites to name a few.

Ferrocement has proven itself as an excellent material for low cost housing. It has high degree of ductility and energy absorbing capacity and has been increasingly used both in terrestrial and marine environments as a structural grade material system, which competes favourably with reinforced concrete and other building materials (Hermosura and Austriaco, 1994; Ramli and Wahab, 1994; Arif, Pankaj and Kaushik, 1999; Arif *et al.*, 2001; Naaman, 2006). Investigations on the use of pre-cast ferrocement elements in low cost housing have proved the effectiveness of the material system under static conditions (Desai and Desai, 1988; Rivas, 1994; Pande, Patil and Waghe, 1997; Olvera *et al.*, 1998). The prefabricated ferrocement elements have also been used successfully in both residential and industrial buildings (Desayi, 1988; Mathew, Prakash and Shaji, 1994; Osorio and Rivas, 1998; Lau *et al.*, 2001).

In this chapter, an attempt has been made to review the studies conducted on ferrocement composites by various investigators. The discussion is divided into three major sections. In the first part, studies related to the strength of ferrocement tested under different

loading conditions have been included. In the second part, mainly durability aspect of the material has been reviewed. In the third part an overview of advancement made in corrosion control through chemical corrosion inhibitors for cementitious composites has been undertaken.

2.1 MECHANICAL BEHAVIOUR OF FERROCEMENT

In this section an attempt has been made to review the earlier investigations carried out by various investigators to understand the behaviour of ferrocement in tension, axial compression, flexure, shear, torsion, fatigue, impact and dynamic conditions of loading.

2.2.1 FERROCEMENT IN TENSION

The tensile strength of ferrocement elements depends upon the distribution and subdivision of the reinforcement in the mortar matrix. However the qualitative behaviour can be understood by studying a typical uniaxial stress strain curve for a ferrocement specimen. Several investigators have reported that when a ferrocement specimen is subjected to increasing tensile stresses, three stages of behaviour are observed (Paul and Pama, 1978; Shah and Balaguru, 1984). In the first stage, the composite behaves like a linear elastic solid. The elastic stage is terminated by the occurrence of the first crack in the matrix. The second stage is termed as the multiple cracking stage. Theoretically, this stage starts at the occurrence of the first crack in the matrix and continues up to the point where wire meshes start yielding. In this range of loading, the number of cracks keeps increasing with an increase in the tensile stress or strain. However, the crack widths increase very little. The increase in strains which occur under larger loads, are distributed through a greater number of cracks instead of widening of the existing cracks. In the third stage, which can be called a crack widening stage, no (or a few) additional cracks are formed. This stage begins when the ferrocement starts to yield and continues up to failure. The number of cracks remains essentially constant and the crack widths keep increasing. The behaviour of the specimen in this stage is primarily controlled by the reinforcement alone.

Akhtaruzzaman and Pama (1988) from their study on cracking behaviour of ferrocement in tension found that the value of slip modulus, ultimate bond strength and modulus of elasticity of mortar has negligible influence on crack spacing. The parameters which significantly influence the crack spacing are the ultimate tensile strength of mortar and volume fraction of mesh reinforcement. The crack width is generally influenced by volume fraction, modulus of elasticity of steel and ultimate bond strength but very small effects are observed for slip modulus, modulus of elasticity of mortar and tensile strength of mortar.

Paramasivam and Ravindrarajah (1988) conducted experimental tests on a series of ferrocement panels. The effect of the reinforcement arrangements on strength and deformational characteristics in direct tension were studied. They concluded that a reinforcement arrangement in which the wire mesh is bundled and placed near the surfaces is better from the point of view of first crack strength, crack width and number of cracks.

Khanzadi and Ramesht (1996) studied the effect of cover and arrangement of reinforcement on the behaviour of ferrocement in tension with particular respect to cracking behaviour. Both first crack strength and ultimate strength were studied. They concluded that under direct tension, the strength of ferrocement at first crack and ultimate load is not affected significantly by the arrangement of the reinforcement. However, specimens having reinforcement evenly distributed with minimum cover showed reduced crack widths and an increased number of small cracks at failure. The contribution of the tensile strength of the mortar and the specimen thickness on first crack strength was found to be significant. On the other hand, these two parameters were found to have negligible influence on ultimate strength.

Ranjbar, Nakassa and Nedwell (1998) investigated galvanized and un-galvanized steel wire meshes with various mesh size and opening in direct tension. They also tested ferrocement specimens employing these wire meshes. It has been concluded that the properties of the individual wires do not adequately identify the performance of welded mesh in ferrocement. The presence of multiple strands appears to improve the performance of mesh.

Abdullah and Mansur (2001) reported the results of 12 ferrocement specimens tested in direct tension. It was concluded from this study that first crack and ultimate load decreases as the angle of wire mesh increases from 0 to 45. It was also found that the increase in transverse reinforcement increases the first crack load but reduces the ultimate load marginally.

Apart from those listed above, a large number of investigators have studied the behaviour of ferrocement in tension. Some of the studies are listed in Table- 2.1.

Table- 2.1 Some Studies on Tension Behaviour of Ferrocement

Investigator(s)	Variables	Properties Investigated
Johnston and Mattar (1976)	Mesh arrangement, type	Tensile strength of Ferrocement
Huq and Pama (1978)	Mesh type, volume fraction	Modification in rule of mixtures
Somayaji and Naaman (1981)	Mesh type, orientation, volume fraction, cover	Stress-strain behaviour, Crack pattern
Somayaji and Shah (1981)	Cross sectional properties	Theoretical model for stress-strain response
Desayi and Rao (1988)	Types of mesh	Statistical analysis of stress-strain behaviour
Walkus (1988)	Loading duration	Load-strain behaviour, Crack and micro-crack study
Pama (1990)	Mesh type	Load-strain and load-orientation characteristics
Desayi and El-Kholy (1991)	Volume Fractions, Modified matrix	Stress-strain characteristics
Arif, Pankaj and Kaushik (1996)	Mesh type, layer, orientation	Ultimate tensile strength of composite

2.2.2 FERROCEMENT IN COMPRESSION

Unlike in tension, the mortar matrix contributes directly to the compressive strength of the composite in proportion to its cross sectional area. Its ultimate strength is due to the contribution of mortar, longitudinal reinforcement (adequately restrained along the length) and confinement provided by the transverse reinforcement in the development of the tri-axial compressive state of stress in the matrix core.

Rao and Rao (1986) carried out tests on hollow specimens in direct compression. The stress strain curve of ferrocement is linear up to 50-60% of ultimate strength and thereafter non-linear and similar to a reinforced concrete specimen in compression. The Poisson's ratio was nearly constant in the linear portion of the stress strain curve and thereafter it increases gradually and reaches maximum value at the ultimate load. A similar variation in Poisson's ratio was also observed by Johnston and Mattar (1976).

Kaushik, Singh and Prasad (1994) carried out experimental tests on twenty five rectangular plates under edge wise compression and observed that for slenderness ratio less than 100, failure is generally due to crushing and splitting of the plates although in some cases buckling might occur, whereas, for slenderness ratio greater than 100, plates invariably fail due to buckling.

Shirai (1998) tested hollow cylindrical ferrocement specimens filled with concrete in compression. Three types of meshes were used for the preparation of specimens. It was concluded that the compressive strength and modulus of elasticity of externally ferrocement bonded concrete increases with rising volume fraction of reinforcement, regardless of the flow of the mortar used as a matrix for ferrocement and slump of the concrete.

Memon, Sumadi and Ramli (2006a) reported the effect of core size and the number of wire mesh layers contained by the ferrocement box to produce ferrocement encased lightweight aerated concrete sandwich. In three types of specimen (Cubes of two different sizes 70.6×70.6×70.6 *mm* & 100×100×100 *mm* and the blocks of 400×200×100 *mm*) were cast and tested. Results show that the compressive strength and density increase with the application of the ferrocement encasement but decrease with the increase in core size. Number of mesh layers is effective in terms of compressive strength and the failure mode however has no significant effect in terms of density.

A few more investigations dealing with compression tests are given in Table- 2.2.

Table- 2.2 Some Studies on Compression Behaviour of Ferrocement

Investigator(s)	Variables	Properties Investigated
Bezukladov *et al.* (1968)	Mesh type	Ultimate strength
Rao and Gowder (1969)	Volume fraction	Elastic modulus in compression
Lee, Raisinghani and Pama (1972)	Mesh arrangement	Elastic modulus in compression
Pama, Sutharatnachaiyaron and Lee (1974)	Mortar	Ultimate Compressive strength
Johnston and Mattar (1976)	Mesh type, volume fraction	Buckling strength
Desayi and Joshi (1976)	Geometry	Compressive strength of wall element
Sandowicz and Grabowski (1981)	Mesh layers and volume fraction	Buckling strength of pipes
Winokur and Rosenthal (1982)	Column geometry	Buckling strength
Ramesh, Seshu and Prabhakar (2003)	Mesh and Fibre	Ultimate strength and ductility

2.2.3 FERROCEMENT IN FLEXURE

The behaviour of ferrocement in flexure is governed by the combined influence of factors that affect its behaviour under tension and compression. Johnston and Mowat (1974) carried out tests on ferrocement beams 150 *mm* wide, 25 *mm* thick, 914 *mm* long and reinforced with meshes of different types and at different orientations. The geometry and the orientation of the reinforcement was found to have a marked effect on the strength of the systems reinforced with expanded metal and welded mesh. For a given effective cross sectional area of steel, expanded metal and welded mesh in their normal orientations perform significantly better than the woven mesh.

Walkus (1975) presented a theory for bending of ferrocement resulting from experimental investigations conducted. Based on the results of experiments, three states of serviceability for ferrocement structures were distinguished and defined by the permissible width of micro-cracks, using the concept of cracking moment and the analogy of the ferrocement behaviour in axial tension, the numerical correlations of stresses, strains and crack widths were established for these states.

Surya Kumar and Sharma (1976) from their tests on ferrocement beams found that the ultimate and first crack strengths of the composite increases linearly with an increase in the percentage area of mesh reinforcement. Based on the test results, the empirical equations were obtained for extreme fibre tensile stress of the composite at first crack and ultimate failure.

Balaguru, Naaman and Shah (1977) conducted tests on ferrocement beams with symmetrical four points loading to predict deflection and crack width. The beams were 130 *mm* wide, 13 *mm* thick and 457 *mm* long. The beams were reinforced with various layers of 12.7×12.7 *mm* woven and welded meshes of 1.07 *mm* wire diameter and 6.35×6.35 *mm* woven mesh of 0.635 *mm* wire diameter. The experimental load deflection curves consisted of three distinct stages, (a) steep linear portion before cracking of mortar; (b) stage after the first cracking of mortar but before yielding of mesh; and (c) portion after yielding of the meshes when the slope becomes almost parallel to the deflection axis. The end of the first stage of the curve corresponds to the first cracking of the mortar. The load at first cracking of the mortar was about the same for the different types and amount of the meshes. This contradicts the results obtained by Logan and Shah (1973). Soon after the first cracking of the mortar, a large number of cracks appeared on the tension face. The cracks ran through the entire width of the beam. The total number of cracks usually equaled the number of transverse wires in specimens reinforced with woven and welded meshes of 12.7×12.7 *mm* size. The location of cracks coincided with the location of transverse wires. This trend was not observed in specimens reinforced with woven mesh of 6.35×6.35 *mm* size except for the groups with six layers, near ultimate load.

Huq and Pama (1978a) analysed the ferrocement elements in flexure by assuming an idealized elastic-perfectly plastic stress-strain diagram of ferrocement in compression and a trilinear stress-strain diagram in tension (Fig. 2.1). Assuming linear distribution of strain across the depth, moments and curvatures were determined for various strain states. Moment-curvature relations were approximated by a trilinear curve and the deflections at various stages of loading were determined using area moment method. The analytically predicted ultimate moment were compared with the experimental results of Balaguru, Naaman and Shah (1977) and were found to be lower. Analytically predicted deflections compared well with the averaged experimental values of Balaguru, Naaman and Shah (1977) in the cracked range but differed in the yield range.

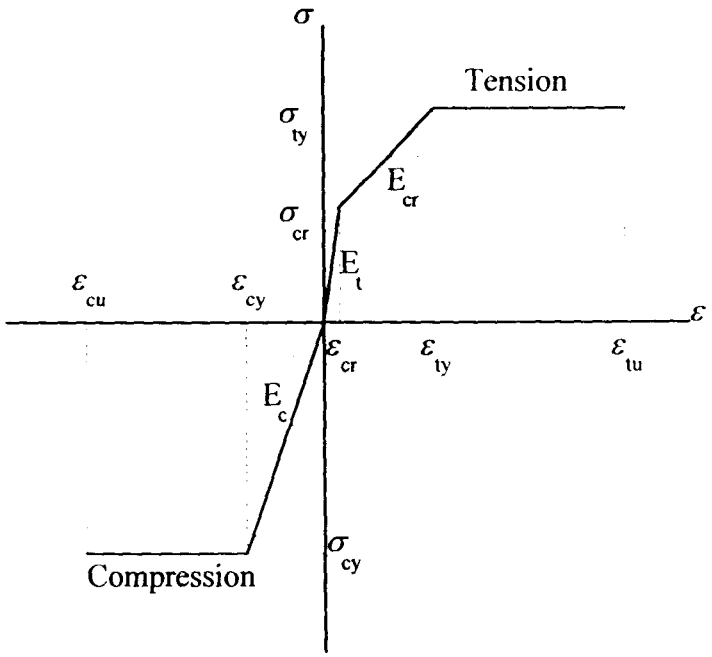

Fig. 2.1 Idealized Stress-Strain Curve for Ferrocement (Huq and Pama, 1978a)

Swamy and Al-wash (1981) studied the deflection and cracking behaviour of ferrocement plates of width 300 *mm* and length 1000 *mm* in flexure. The type and amount of mesh reinforcement, mortar cover and thickness of the section were the main variables. The mortar matrix incorporated flyash as a replacement of both cement and fine aggregate. Mild steel mesh and high tensile steel mesh were the two types of reinforcements used. The specimens with mild steel mesh reinforcement showed three stages in the load-deflection curve, namely, the elastic, cracked and yielded stages, whereas in high tensile steel mesh reinforced specimens, these three stages can be identified distinctly in only those specimens which were reinforced with up to four mesh layers. The specimens reinforced with high tensile steel gave reduced crack spacing and crack width at failure.

The average crack spacing stabilized in mild steel and high tensile steel reinforced specimens at specific surface values of about 0.2 per *mm* and 0.15 per *mm* respectively. The crack spacing was influenced to some extent by the mesh opening, mortar cover and section thickness. Based on the concept of plastic analysis, a simple method to predict the ultimate moment capacity was proposed. The method gave satisfactory prediction of ultimate moments of experimental investigations as well as the test results of Logan and Shah (1973).

Mansur and Paramasivam (1985) investigated the behaviour of ferrocement beams by varying the volume fraction of reinforcement and water-cement ratio of mortar. They found that both the first crack and ultimate moments increase with an increase in either the matrix grade (by decreasing the water-cement ratio) or the volume fraction of reinforcement. For a given volume fraction of reinforcement, a lower grade matrix gives large number of cracks with smaller crack widths. However, as the load approaches the ultimate value, the cracks open up more rapidly. For a given grade of matrix, higher volume fraction of reinforcement provides more effective control of crack width.

Clarke and Sharma (1988, 1991) presented a strength analysis for ferrocement plates under flexural loading based on classical lamination theory. The ferrocement plate was considered as a laminated fibre reinforced composite material composed of generally orthotropic laminae. Through the slab thickness, variable parameters *viz.* number of mesh layers, mesh orientation and pattern of mesh layers were incorporated. A comparison of analytical test results was made with the experimental results. They concluded that the lamination theory can be used with full confidence for the analysis of ferrocement plates.

Arif, Kaushik and Pankaj (1998) carried out tests on ferrocement slabs under three point flexural loading. Test variables include the type of wire meshes (woven and welded), number of mesh layers and mesh orientation pattern. It was observed that orientation scheme does not cause a significant variation in response. Two different mathematical models *viz.* homogeneous layered model and mortar-ferrocement layered model were proposed. Both the proposed models match the experimental results well in the elastic range. In the post elastic range the mortar-ferrocement layered model is found to predict the load-deflection response best.

Nassif, Chirravuri and Sanders (1998) investigated the flexural behaviour of composite beams made of reinforced concrete overlaid on a thin section of ferrocement. Variables were types of mesh and number of layers of mesh. Beams were tested under a two point loading system. Results show that the proposed composite beams have better ductility and cracking strength than conventional reinforced concrete beams.

Islam, Maity and Kalita (2002) performed simulation of deflection and stress behaviour of different types of roofing element using finite element method. Theoretical values of roofing element so obtained were compared with experimental results. Economic shape in the form of shell was suggested.

Bhattacharrya, Tan and Mansur (2003) explored the use of hollow sandwiched ferrocement panels. Based on strain compatibility, design charts relating the flexural moment capacity of ferrocement hollow sandwiched panel system to the mortar strength, steel strength, panel thickness and overall section depth, were developed.

Hossain, and Tsukioka (2006) developed design equation for flexural Young's modulus of thin cement composites reinforced with different types of wire meshes. An experimental investigation on the flexural behavior of thin cement composite elements reinforced with different types of wire meshes with varying number of mesh layers as well as varying percentage of effective reinforcement was carried out. The experimental specimens were tested under two points loading condition for understanding the basic mechanical behavior of cement composites such as Young's modulus in flexure. By analyzing experimental data, a general equation for the determination of Young's modulus of the cement composite containing different wire meshes is proposed. In addition to the experimental investigation, a flexural section of thin cement composite is also theoretically analyzed for the validity of the proposed equation. It is revealed that the proposed equation gives better estimation of flexural Young's modulus of cement composite as compared to the available analytical equations.

Jagannathan and Sundarajan (2006) studied the effect of polypropylene fibres on the mortar matrix with respect to workability and strength. Flexural behaviour of ferrocement panels reinforced with a commercially available polymeric mesh (3-5 layers) and incorporating polypropylene fibres (0.5% – 2.5%) were experimentally investigated.

The results were compared with ferrocement panels not containing such fibres. It was found that there is considerable reduction in the crack-width and deflection and improvement in the 'mode of failure' that are uniquely attributed to the positive role of fibres in ferrocement panel.

Memon, Sumadi and Ramli (2006) tested prisms of standard size, made of lightweight aerated concrete (AC) encased in ferrocement, to investigate the flexural strength. The results show that the encasement of the aerated concrete with ferrocement significantly improves the flexural strength. The improvement is proportional to the number of the layers of wire mesh and the density of the core.

Table- 2.3 lists some more research studies conducted on ferrocement elements in flexure.

Table- 2.3 Some Studies on Flexural Behaviour of Ferrocement

Investigator(s)	**Variables**	**Properties Investigated**
Balaguru (1981)	Mesh specific surface, type, volume fraction	Crack spacing and curvature
Kaushik, Trikha and Kotdawala (1981)	Support condition	Flexural strength
Swamy and Spanos (1985)	Mesh type, volume fraction	Deflection and cracking behaviour
Paramasivam and Ravindrarajah (1988)	Mesh arrangements	Strength and deformation characteristics
Shirai and Ohama (1988)	Volume fraction, mortar type	Flexural behaviour
Vaidyanathan and Perumal (1988)	Mortar modulus	Analytical expression in flexure
Al-Rifaie and Trikha (1990)	Mesh type, arrangement	First crack moment and ultimate moment capacity
Ballarin and Hanai (1992)	Geometry of slab specimen	Ultimate load carrying capacity and deflection
Saini, Sehgal and Sharma (1996)	Mesh type, arrangement	Analytical modeling
Nedwell and Nakassa (1998)	Mesh type, modified mortar	Ultimate moment carrying capacity

2.2.4 FERROCEMENT IN SHEAR AND TORSION

Research to evaluate the shear strength of ferrocement has been limited. Most applications of ferrocement have been in structural elements where tensile strength or crack width is the governing design criterion. Ferrocement panels used for roofing purpose, normally have a large span/depth ratio in flexure which precludes shear as a failure criterion. Collen and Kirwan (1959) tested ferrocement specimens reinforced with woven mesh and skeletal bars in bending at a shear span to depth ratio of 0.4. The shear strength of ferrocement elements was found to be 35% of their flexural strength over a fairly wide range of steel contents (288-480 kg/m^3).

Mansur and Ong (1987); Krishna and Gouda (1988) found that the shear strength of ferrocement depends upon the strength of mortar, volume fraction and strength of the wire mesh. The shear strength of ferrocement beams with welded wire mesh was found to be more than the shear strength of beams reinforced with woven or hexagonal wire meshes because of the breaking strength of welded wire mesh being higher than that of woven or hexagonal wire mesh.

Due to the low out-of-plane stiffness, ferrocement is mostly used in shell like structures. However, attempts have been made to eliminate this weakness by altering the geometrical form of element such as I, channel, box and sandwich sections etc. When such a section is loaded transversely, it may undergo bending, shear, torsion or combination thereof. Researchers have studied the behavior of these elements under bending and shear and proposed prediction equations for their ultimate strengths. However, a little information is available on torsional behavior of such sections.

Arora and Rao (2006) developed an analytical model to calculate the ultimate torsional strength of ferrocement hollow box section under pure torsion. Seven ferrocement hollow box specimens were cast with varying parameters and their ultimate strength is compared with predicted values. It was verified that the proposed model is able to predict the ultimate torsional strength and corresponding angle of twist of ferrocement hollow box sections with good accuracy.

Mansur (2006) conducted torsion test on ferrocement members of tubular cross section in which the volume fraction of reinforcement, V_f and wall thickness, t, were varied. Test results indicate that while the un-cracked stiffness remains unaffected, an increase in either V_f or t, increases both the post cracking torsional stiffness and ultimate strength, but decreases torsional ductility. Introducing material laws appropriate to ferrocement the 'softened truss model' for conventional reinforced concrete beams was modified, and complete torque-twist curves were derived and compared with test results. In general, a good agreement is obtained.

Some more research findings dealing with shear and torsional behaviour of ferrocement are presented in Table- 2.4.

Table- 2.4 Some Studies on Shear and Torsional Behaviour of Ferrocement

Investigator(s)	Variables	Properties Investigated
Vaidyanathan and Perumal (1988)	Volume fraction, geometry	Empirical relation for the ultimate shear capacity
Ahmad and Nimityongskul (1998)	Mesh layer	Punching shear capacity
Mansur, Ahmad and Paramasivam (1998)	Size of patch load, mortar strength, thickness of slab, volume fraction	Punching shear capacity
Mansur and Kiritharan (2001)	Shear span to depth ratio, volume fraction, mortar strength	Ultimate load carrying capacity
Kumar and Desai (2001)	Compressive of mortar strength, longitudinal steel, shear span to depth ratio	Design shear stress

2.2.5 FERROCEMENT IN FATIGUE

The fatigue behaviour of ferrocement has been found to depend upon the fatigue properties of the reinforcement. Research investigations on behaviour of ferrocement units under fatigue have predominantly been undertaken under flexural loading conditions.

Greenius (1975) concluded that ferrocement can withstand repeated stresses of 12.3 *MPa* for 2×10^5 *cycles*. This stress represents 65% of the cracking stress. It was also observed that fatigue tests cannot eliminate creep due to which the apparent modulus of elasticity drops. The stresses dropped by about 20% to 50% of the initial stress amplitude under a constant strain test.

Balaguru, Naaman and Shah (1979) studied the fatigue life, deflection and crack widths of ferrocement beams reinforced with square welded and woven meshes. The beams were subjected to load levels of ±40%, ±50% and ±60% of the yield load capacity of the specimens. The failure of specimens was observed to be due to the fracture of the extreme layer of wire mesh. Based on the test results, the fatigue life (N_f) was predicted by the following equation

$$S_r = 0.6433 - 0.1345 \log_{10} N_f \tag{2.1}$$

where N_f is the fatigue life in *kilocycles* and S_r is factor representing stress range in the extreme layer of wire mesh in *MPa* calculated on the basis of cracked elastic section.

Paramasivam, Das Gupta and Lee (1981) investigated the fatigue strength for different volume fractions of galvanized square woven meshes. They found that the failure load for all the specimens at 10^6 *cycles* was about 45% of their ultimate static load. It was also observed that the cracks in the specimens failing by fatigue were much fewer and wider than specimens that failed under static loads.

Raisinghani and Sai (1984) studied the fatigue behaviour of ferrocement slabs under pulsating loads. All the slabs were reinforced with various layers of chicken wire mesh. The lower load limit of the pulsating machine was about 130% to 180% of the first crack load of the specimens. For specimens subjected to the upper load level which was much less than the ultimate static load, the residual deformations first increased as the number of load cycles increased, then reached a stable condition and again increased with load cycles till the fracture occurred. Such specimens withstood 1×10^6 to 3×10^6 *cycles*. Those specimens that failed within 10^6 *cycles*, exhibited a continuous increase in the residual deformation.

Lin *et al.* (2006) studied the fatigue strength of hybrid ferrocement manhole covers and conventional ferrocement manhole covers experimentally by generating *S-N* curves. Hybrid ferrocement manhole covers were reinforced with commercial steel fibers taken 2% by volume and conventional ferrocement manhole covers were reinforced without steel fibers. The skeletal steel and wire meshes were kept constant for both types of covers. High strength mortar of 14 *days* compressive strength 70 *MPa* was used for both types of covers. Four specimens from both types of covers were tested under static flexural test with central line load and the mean values of these ultimate static loads were subsequently used for establishing the fatigue test loading. Fourteen specimens from both types of covers were tested under fatigue. The peak loads were kept at 85%, 80%, 75% and 65% of the ultimate static load respectively.

The test results showed that the addition of steel fibers increased the flexural fatigue strength of the ferrocement manhole covers. It was found that the maximum percentages of ultimate static loads causing failure at two million cycles were approximately 67.55% and 64.23% for hybrid and conventional ferrocement respectively. In terms of expected number of cycles to failure, the hybrid ferrocement cover is 120% stronger than conventional ferrocement cover. The results showed that fatigue strength of ferrocement manhole covers could be improved by the inclusion of randomly oriented short steel fibers in the mortar matrix.

A few more studies dealing with fatigue tests are given in Table- 2.5.

Table- 2.5 Some Studies on Fatigue Behaviour of Ferrocement

Investigator(s)	**Variables**	**Properties Investigated**
Picard and Lachance (1974)	Mesh type, arrangement	*S-N* relationship
Karasudhi, Mathew and Nimityongskul (1977)	Mesh type	*S-N* relationship
Bennet, Fakhri and Singh (1985)	Size of patch load, mortar strength, thickness of slab, volume fraction	Fatigue behaviour of ferrocement
Xiong and Singh (1992)	Mesh type, arrangement	*P-S-N* relationship
Desayi and Suresh (1994)	Mesh type, arrangement	Deflection, strain, curvature and ductility

2.2.6 FERROCEMENT IN IMPACT

The impact resistance of ferrocement is found to depend on the specific surface, strength and type of reinforcement and the thickness of the element. Bezukladov *et al.* (1968) compared the impact strength of reinforced concrete and ferrocement plates by using a falling weight on the plate. They found that the dispersion of reinforcement promotes increase in the impact strength. While reinforced concrete plates had large cleaving, the crushed mortar in ferrocement is held back by the meshes from disintegrating. Shah and Key (1972) observed that the damage to the ferrocement plates decreased with an increase in specific surface or the strength of the mesh reinforcement. Greenius and Smith (1972) found that the provision of skeletal steel bars along with mesh reinforcement improved the strength and deformability characteristics under impact. Burgess and Allen (1974) found that the increase in thickness of ferrocement increases the impact resistance. Nimityongskul, Bor-Shiun and Karasudhi (1980) found that the impact resistance increases with the increase in steel content or the specific surface of mesh reinforcement. It was observed that under an almost practical maximum steel content condition, the impact resistance does not always increase with an increase in the specific surface of mesh reinforcement. Rao *et al.* (1981) found that the specimens reinforced with welded meshes offer the highest impact resistance followed by woven and chicken wire meshes for a given steel percentage.

Mathews (1982) tested ferrocement slabs subjected to impact by dropping spherical, cylindrical and conical projectiles, and also conducted the Charpy Impact test on beams. It was concluded that impact strength increases with volume fraction of steel V_f and surface ratio of steel S_R. For a welded wire ferrocement slab, the Charpy Impact strength I, was proposed in the form of the empirical relationship

$$I = \left(3.09 \times 10^{-4} V_f f_y - 63.04\right) \qquad N\text{-}mm/mm^2 \qquad (2.2)$$

Khan, Ong and Paramasivam (2001) evaluated the performance of square shaped ferrocement slabs of 1000 *mm* size and 30 *mm* thickness, subjected to low velocity projectile impact, under simply supported condition, using an instrumented drop weight test facility. The slabs with fibre sustained less damage at the impact point and the failure was localized compared to slabs without fibres.

Alwis *et al.* (2001) studied the behaviour of steel-cementitious composite sandwiched plates of 300 × 300 *mm* in size under low velocity impact. A 40 *kg* drop hammer with hemispherical head, under free fall height of 4*m* was used to create the impact. The results showed large permanent deformation in the steel cover plates but no fracture. Middle plates of normal and high strength concrete cracked into pieces under this kind of impact. Introduction of a ferrocement or SIFCON layer to the middle plate reduced the steel strains and also prevented disintegration of the middle plate.

Eswaramoorthi and Subramanian (2006) developed a simple, portable, and practical test to perform impact study suitable for fiber reinforced concrete and fibrous ferrocement slabs. The number of impact blows delivered by a drop hammer is accumulated until the first visible crack occurs and until the test specimen is forced to separate by continued impacting. Different fibers with different volume ratios are adopted and the responses like energy absorption, deflections etc. are obtained and the results are compared with the results obtained from *ANSYS* Software. It was verified that the impact energy required to cause failure of ferrocement is 60% more than that of concrete. Some more studies are listed in Table- 2.6.

Table- 2.6 Some Studies on Impact Behaviour of Ferrocement

Investigator(s)	Variables	Properties Investigated
Grabowski (1985)	Mesh type, section thickness	Crack spacing and crack width
Shirai and Ohama (1988)	Mesh volume fraction and matrix	Improvements in impact resistance
Grabowski and Radomski (1988)	Mesh type	Failure mode under impact
Alwis and Paramasivam (2004)	Mesh type, arrangement	Stress-strain relationship

2.2.7 FERROCEMENT UNDER DYNAMIC LOADING

Even though ferrocement is in use for a long time, it has rarely been utilized to its full potential. The fact that the ferrocement has a great deal of ductility and energy absorption is yet to be fully exploited. The awareness that ferrocement can be an effective material for a terrestrial dynamic environment is slowly on the rise. Little research activity has so far been initiated in this area.

Reinhorn and Prawel (1986) probably made first use of ferrocement in a large shaking table facility built at the State University of New York at Buffalo. The ferrocement was found to be particularly useful for the table surface. Its unique characteristics led to a very thin yet stiff facing which greatly improved the overall dynamic behaviour of the system. The use of ferrocement was found to be advantageous because of the ease of construction and improved tensile properties, crack control, reduced dimensions and light weight as compared with similar structures made of reinforced or pre-stressed concrete.

Neelamegam and Sekar (1991) conducted free vibration tests on ferrocement slabs. Natural frequency and damping, the essential dynamic characteristics of any structural system were obtained. Their theoretical computations indicated that natural frequency of the ferrocement slab decreased with the increase of reinforcement in the slab. The natural frequency was observed to be influenced by the amount of cracking and flexibility of support frames. The damping in the slabs decreases with increase in the percentage of reinforcement for both the un-cracked and cracked specimens. They also observed that cracking in ferrocement slabs does not alter natural frequency of the system.

Arif, Pankaj and Kaushik (1996a) carried out the free vibration analysis of ferrocement plates by employing a macro-mechanics based approach. The vibration characteristics were obtained using closed form solution with different assumptions and numerical solution using finite element method, with lumped and consistent mass matrices. The effect on fundamental frequency due to change of orientation, moduli ratio, aspect ratio and stacking arrangements were studied.

2.3 DURABILITY OF FERROCEMENT

It is clear from the previous section, that over the years, the ferrocement has proven itself as an excellent construction material. But the successful performance of ferrocement depends to a great extent on its durability against the environment than on its strength properties. For ferrocement to be durable, its component materials, namely cement mortar and wire mesh reinforcement should not only retain their bond and strength but also not disintegrate over a period of time. The reduction in the durability of composite can be attributed to the deterioration of matrix as well as of the reinforcement.

The disintegration of mortar is due to volume change caused by various weathering agents such as cyclic thermal changes and alternate wetting and drying. The action of aggressive chemicals on hardened cement paste, particularly sulfates, causes volume changes and cracks in the mortar. Alexander (1987) suggested that the pH value of ferrocement mortar should be more than 11 and that any action which diminishes the pH value should be avoided.

The exact nature of the corrosion, which can occur in ferrocement is quite complex. It is clear, however, that corrosion can and does take place in ferrocement, if certain conditions are present. Steel corrosion in ferrocement like steel corrosion in reinforced concrete is mainly an electrochemical process which occurs in an aqueous environment. Water is necessary for electrolyte constitution and is always present in mortar. Cement mortar offers more protection against corrosion of steel wire mesh in ferrocement structures when the mix is designed for maximum strength and water tightness such as in mortars with low water cement ratio. Mortar cover over the reinforcement may be thin but of high cement contents, thereby preventing the corrosion of reinforcement by providing physical and chemical protection. Strength and water tightness provides physical protection while calcium hydroxide provides chemical protection against aggressive environment. Factors that are responsible for the effectiveness of cement mortar to prevent corrosion are: high cement-sand ratio, low water-cement ratio, high quality aggregate and enough workability to minimize voids (Chalisgaonkar, 1987).

A number of case studies dealing with the current status of the previously built ferrocement structure or structural component are reported in literature. These studies have been reviewed here. The idea is that the information regarding these structures will help in understanding the problem of durability of ferrocement in general and corrosion of ferrocement reinforcement in particular.

Trikha *et al.* (1984) investigated the extent of corrosion in 12 ferrocement structures of various types with ages ranging from 6 to 12 *years*. They concluded that in the mechanically cast ferrocement structures using galvanized steel mesh and well graded sand for mortar, corrosion is only mild with or without protective coating. However, inadequate cover, bad compaction and poor workmanship all lead to an increase in the incidence and rate of corrosion.

Kaushik *et al.* (1988) observed the deterioration in the condition of several ferrocement structures cast during the period from 1972-87, which were subjected to the environmental conditions of various degrees. Incidence of corrosion was continuously monitored. A few structures were in cracked state with their meshes exposed over the years. They observed that the incidence of corrosion has in general almost doubled over a period of three years, since the samples were first drawn. The corrosion was found to be more in meshes which were in direct contact with the environment.

Alexander (1989) compared the parameters influencing the durability of ferrocement with that of reinforced cement concrete. He concluded that the behaviour of reinforced concrete and ferrocement with regard to the phenomenon of durability differs only in the degree of protection provided by their assembly. The superior resistance of ferrocement to invading acid ions and gaseous CO_2 is probably due to the use of the galvanized steel, fine grained well-graded sand, low water cement ratios, chemical neutralization by the alkalinity of rich mortars, and to compaction which is readily obtained as a consequence of the reduced mass of the ferrocement. However these parameters are found to be ineffective in reducing the long term diffusion of moisture, CO_2 or chloride ion into the matrix. A carbonation study was also undertaken which showed that CO_2 penetration reached depths of 5 *mm* to 15 *mm* for a 15 *year* equivalent exposure with the lower figure applying to specimen with coated surface.

Mansur *et al.* (1996) investigated the condition of a thirteen year old ferrocement structure which had been left abandoned for past four years, at the time of observation. A part of the structure was cut out and tests were performed to determine the depth of carbonation, extent of chloride-ion penetration, state of the embedded reinforcement and strength characteristics of the composite in tension, compression and flexure. The results revealed that the structure still retained the desired strength but due to inadequate maintenance and lack of protective surface coating, it showed some signs of degradation due to corrosion of reinforcement.

2.3.1 BEHAVIOUR IN AGGRESSIVE ENVIRONMENT

The corrosion and durability aspect of ferrocement in the aggressive environment has been a major concern among the researchers working in the area of ferrocement. Mathew, Achutya and Rao (1984) subjected cracked ferrocement specimens to accelerated corrosion tests by alternate wetting and drying using sea water for thirty days. They found that the ultimate tensile strength of the specimens, with initial crack-widths of about 0.05 *mm* and 0.10 *mm*, was reduced by 4% and 12 % respectively.

Chowdhury and Nimityongskul (1985) studied the corrosion in cracked and un-cracked ferrocement specimen by subjecting them to alternate wetting and drying in sea water and urine. The depth of mortar cover was the main variable. A considerable improvement in the corrosion protection was obtained by increasing the depth of cover from 1 *mm* to 3 *mm* and very small improvement was obtained beyond 4 *mm*. The presence of crack is contributory factor for small covers and their effect becomes negligible when cover thickness is 4 *mm* or higher. The intensity of corrosion is higher in the case of urine than sea water. With 4 *mm* depth of cover, the degree of corrosion comes down to the same level as that for sea water.

Ravindrarajah and Paramasivam (1985) studied the effects of alternate drying and wetting in sea water and of curing in 6% *NaCl* solution on the strength and stiffness of ferrocement in direct tension and flexure. The test results indicated that the ultimate strength and stiffness of ferrocement were not affected by 1000 *cycles* of drying and wetting in sea water or by exposing in 6% *NaCl* solution for 9 *weeks*. However, the first crack strength showed improvement due to maturity gain for the mortar component. The ferrocement specimen initially subjected to first crack load did not suffer any loss in the ultimate strength due to the above exposure conditions.

Selvi Rajkumari *et al.* (1985) studied the corrosion resistance of polymer impregnated ferrocement and un-impregnated ferrocement specimens. Accelerated corrosion tests were performed by subjecting the specimens to alternate drying and wetting in salt water (3.5% *NaCl*). The corrosion damage of un-impregnated ferrocement specimens was found to be nearly 10 times more than in the polymer impregnated ferrocement specimens. The durability of ferrocement can also be improved by mixing an acrylic latex solution or by coating ferrocement surface by appropriate paints (Iorns, 1984; Sharma, 1985).

Gorska (1985) compared the properties of concrete, plain ferrocement and methyl methacrylate monomer (*MMA*) pipes subjected to simulated acidic medium with 4-pH value and sulphate medium with 10% Na_2SO_4 solutions. Testing of the specimens consisted of determining changes in tensile strength; absorbability and appearance after 3, 6 and 12 *months* of exposure and the results were compared with the specimens in natural sewage environment. Results showed that the *MMA*-impregnated ferrocement specimens in comparison to un-impregnated ones are characterized by higher tensile strength and four times lower absorbability. The strength properties of plain ferrocement are stable with a slight tendency to increase over a period of time. A decrease in the absorbability of these specimens was also observed.

Yozuqullu (1986) studied the durability of sulphur impregnated ferrocement specimens. These specimens were found to be practically impermeable with a noticeable increase in strength together with an improved resistance against acid attack.

Lukita, Austriaco and Nimityongskul (1987) investigated the corrosion of wire mesh in ferrocement specimens subjected to simulated corrosive environment. The actual marine environment was simulated by 16 *hours* immersion in sea water and 8 *hours* drying in laboratory environment. The immersion cycles were ranged between 10-20 *cycles*. Variables chosen for study were thickness of mortar layer, type of cement and surface condition of wire mesh. Test results revealed that for un-galvanized and galvanized wire meshes, a mortar cover of 4 *mm* and 3 *mm* respectively, could provide sufficient protection for ferrocement structures. It was also concluded that the addition of 10% rice husk ash makes mortar reasonably impervious and helps in controlling the corrosion.

Rengaswamy *et al.* (1987) investigated the usefulness of rebar potential measurements in monitoring the corrosion. It was concluded that the use of monitoring the reinforcement corrosion by potential measurement is limited due to the influence of moisture content. In submerged zone this criteria was not reliable, however in structures exposed to open atmosphere and splash zone, a potential value nobler than –200 *mV vs SCE* may be indicative of passive condition. It was further observed that the tolerable limit for chloride is around 1000 *ppm* by weight of concrete irrespective of strength.

Ramli (1988) studied the fatigue behaviour of ferrocement specimens of size 350×125×30 *mm* with 7 layers of woven wire mesh of 0.71 *mm* diameter subjected to marine environment. The test result indicates higher fatigue strength under continuous exposure in sea water which was attributed to the wedging effect by salt deposit which prevents the further crack development.

Ramesht, Vickridge and Jafer (1993) performed tests on corrosion performance of ferrocement specimen exposed to extremely aggressive environment (6% *NaCl* solution). Parameters studied were arrangement of mesh reinforcement and depth of the mortar cover to the mesh. It was found that both un-galvanized and galvanized layers of wire meshes sustained some degree of corrosion. It was further concluded that the depth of mortar cover over the mesh layer is an important factor in reducing the corrosion rate of the embedded steel mesh.

Mathews, Sudhakumar and Jayasree (1993) tested ferrocement specimens in axial tension subjected to simulated marine environment. The parameters chosen for the investigation were water cement ratio, sand cement ratio and the dose of water reducing admixtures. The degree of corrosion was assessed by reduction in ultimate tensile strength. It was concluded that the specimen subjected to accelerated exposure suffered appreciable loss of strength as compared to specimen kept in open atmosphere.

Ramesht (1995) carried out flexural tests on ferrocement plate specimen of size 350×120×38 *mm*, subjected to normal as well as simulated corrosive environmental conditions. It was concluded that the presence of saline environment increases the brittleness of mortar, reduces the number of cracks and increases the crack width. The reduction in the strength of ferrocement specimens with ungalvanised wire mesh was found to be greater than specimens with galvanized meshes due to corrosion.

Vickridge, Nakassa and Turner (1998) reported the results of plate specimens cast with modified mortar prepared using three different mineral admixtures namely silica fume, ground granulated blast-furnace slag and pulverized fly ash. These specimens cast with both galvanized and un-galvanized wire meshes were cured for 7 *days* and then left for 21 *days* for air drying, after which all faces except one were coated with an epoxy.

The specimens were then exposed to extremely aggressive environment (6-7% *NaCl* solution) for a period of six *months*. The results indicated that the admixtures studied, particularly silica fume can provide a low permeability mortar capable of preventing the penetration of chlorides or other detrimental solutions into the mortar and reducing corrosion damage. It was further noticed that both galvanized and un-galvanized meshes sustained some degree of corrosion.

Vickridge and Ranjbar (1998) performed tests on ferrocement plates subjected to wet-dry simulator in 6% *NaCl* solution. The specimens were exposed to a total of 3600 wet and dry cycles, each cycle consisting of 30 *minutes* wet phase and 30 *minutes* dry phase. The variables studied were volume fraction, water cement ratio, mortar mixtures and type of meshes. The results revealed the important role of water cement ratio in controlling the durability as both the first crack and the ultimate load increase with the decreasing water-cement ratio and increasing volume fraction of reinforcement. The specimen with both galvanized and un-galvanized wire meshes, cast with low water-cement ratio exhibited less corrosion.

Vickridge and Ranjbar (1998a) monitored the corrosion performance of reinforcement in ferrocement specimen exposed to corrosive environment. Both virgin and tested (cracked) specimens were subjected to six months of exposure. Corrosion potential and linear polarization resistance were observed on a monthly basis. It was found that the specimen with thick cover whether virgin or cracked, sustained lower corrosion. It was further observed that all cracked specimens sustained higher degree of corrosion than virgin/un-cracked specimen, which demonstrates that the cracks even very small ones have a significant effect on the corrosion activity.

Mehdi and Ahmad (1999) conducted tests on ferrocement specimens exposed to Karachi sea water under accelerated laboratory test. Flexural tests were conducted on rectangular plates and the tensile behaviour was observed through dumb-bell shaped specimen. The results showed that the sea water reduces the tensile and flexural strength. In another study, with the similar specimens, Mehdi and Ahmad (2000) reported a reduction of 13% and 11% in tensile strength and flexural strength respectively, when exposed to sea water for a period of 30 *days* in summer.

Masood *et al.* (2003) conducted tests on rectangular ferrocement panels exposed to normal, moderate and aggressive environment. These panels were tested in flexure after 1 *month* of exposure. The variables undertaken for this study were type of mesh, normal and fly ash modified mortar. It was concluded that the addition of fly ash in mortar increases the flexural strength. Wire mesh exhibited corrosion even in 1 *month* exposure time under both moderate and aggressive environment.

2.3.2 IMPROVEMENT IN DURABILITY

Improvement in durability of ferrocement broadly means improvement in its ability to resist weathering action, chemical attack, abrasion, cracking and any other process of destruction such as corrosion. In this section, a review of the investigations undertaken by various researchers to enhance the durability and thereby, the service life of the ferrocement structures, has been made.

2.3.2.1 PREVALENT TECHNIQUES

Various investigators have suggested the use of galvanized wire mesh as one of the way to delay the onset of corrosion (Biggs, 1972; Trikha *et al.* 1984; Ramesht, 1995). However, it was found that both un-galvanized and galvanized layers of wire mesh sustain some degree of corrosion during prolonged exposure even in normal environment (Ramesh, Vickridge and Jafer, 1993; Ramesht, 1995; Mansur *et al.*, 1996; Vickridge and Ranjbar, 1998).

Mortar cover to the wire mesh reinforcement in ferrocement is another important parameter which improves the durability. The cover in ferrocement elements is about 2 *mm* to 5 *mm* which increases the corrosion risk to mesh reinforcement. Several investigators found that relatively thick mortar cover to the mesh reinforcement in ferrocement improves the resistance against corrosion (Turner, 1983; Chowdhury and Nimityongskul, 1985; Lukita, Austriaco and Nimityongskul, 1987; Ramesht, Vickridge and Jafer, 1993; Vickridge and Ranjbar, 1998a), although, Naaman and Sabnis (1978) suggested a net cover of only 2 *mm*. They even suggested a smaller depth of cover for those ferrocement elements in which reinforcement was galvanized, surface painting was used and low limiting crack width was adopted. If the cracks are not wider than 0.1 *mm*, Greenius (1973) found that the corrosion was moderate even when the depth of cover was 0.5 *mm*.

Use of dense mortar has also been reported as one of the solution techniques to control corrosion, thereby, providing relatively an impervious layer of cover to the reinforcement. Several investigators recommended use of well graded fine aggregate (Trikha *et al.*, 1984; Youzuqullu, 1986). Addition of admixtures like fly ash, silica fume, ricehusk ash *etc.* has also been suggested as one of the ways of achieving dense mortar (Lukita, Austriaco and Nimityongskul, 1987; Vickridge, Nakassa and Turner, 1998; Masood *et al.*, 2003).

Iorns (1987) suggested the use of high strength mortar which can be achieved with a water cement ratio below 0.4 and a sand cement ratio below 2.0. The desired workability should be achieved by adjusting the sand content and not the water cement ratio. The idea was to cover all reinforcement completely coated with a non-porous mortar. These recommendations were found to be effective over a considerable period of time in towboat construction industry.

Parvez and Austriaco (1987) reviewed the state of understanding of the corrosion and its prevention in ferrocement. On the basis of studies carried out by a number of investigators they concluded that research on corrosion till date has not produced a steel or other type of reinforcement which will not corrode when used in concrete or ferrocement. They further observed that the onset of corrosion can be delayed / controlled by correct construction practice, careful attention to detailed design, proper and appropriate choice of preventive measures, repairing techniques and quality control of work.

Use of chemical admixture for the control of corrosion in ferrocement has been explored by a very few investigators. The use of galvanized wire mesh along with the un-galvanized skeletal steel bars creates galvanic cell problem. Christensen and Williamson (1971) were first to identify this problem and also gave the solution. They suggested the use of chromium trioxide at the rate of 100-300 *ppm* by weight of water in preparing the mortar. Iorns (1984) also reported the use of chromium trioxide as an inhibitor of hydrogen gas generation when galvanized mesh is used in ferrocement. Rengaswamy, Saraswathy and Balakrishnan (1992) recommended the use of a patented admixture inhibitor consisting of one or more of the chemicals, namely trisodium phosphate, sodium nitrite, sodium hydroxide and sodium carbonate, for the protection of reinforcement against corrosion due to chloride concentration in ferrocement.

Shirai and Ohama (1995) reported the performance of ferrocement with polymer-modified coating on reinforcement. The coating paste was prepared using styrene-butadiene rubber latex. It was concluded that the corrosion inhibiting property is remarkably improved.

2.3.2.2 ACI RECOMMENDATIONS

Although the measures required to ensure durability in conventionally reinforced concrete also equally apply to ferrocement, three other factors that are unique to the ferrocement, have been identified by American Concrete Institute Manual (ACI-549 R, 2003). First, the cover is small and consequently it is relatively easy for corrosive liquids to reach the reinforcement. Second, the surface area of the reinforcement is usually high, so the areas of contact over which corrosion reaction can take place, and the resulting rate of corrosion, are potentially high. Third, although the steel reinforcement used in ferrocement is generally galvanized to suppress corrosion, the zinc coating may have adverse affect from gas bubble generation.

Further, to improve the durability of ferrocement following recommendations have been made:

- Use of galvanized reinforcement
- Steps to minimize water content
- Use of chemical and mineral admixtures to minimize permeability
- Use of proven appropriate coating.

Apart from this, it is finally recommended in the ferrocement section of ACI that "durable and long term sealants are needed for ferrocement, especially in marine applications, to prevent the penetration of water and salt that could lead to corrosion of reinforcing mesh. Although several methods, such as laminating techniques, are available to ensure void cavity free ferrocement, further work is needed to cover different site and construction requirement". As per ACI-222 (1996), use of corrosion inhibitors has also been recommended for concrete which can be extended to ferrocement as well.

2.4 CORROSION CONTROL THROUGH CHEMICAL CORROSION INHIBITORS

Despite the fact the corrosion inhibitors are being widely used for the corrosion control in concrete composites, it's use for the ferrocement composites has not yet attracted the attention of the many research investigators. A very few investigations are reported in the literature which have been reviewed in previous section. However, realizing the fact that the corrosion process in ferrocement composites is almost similar to that associated with the conventional reinforced concrete, in this section, an attempt has been made to review the advancements made in the field of corrosion control in concrete composites through chemical corrosion inhibitors.

During the last few decades the corrosion problem in reinforced concrete has been extensively investigated by many researchers. Corrosion inhibitors are one of the most cost-effective solutions to rebar corrosion problem in concrete. Corrosion inhibiting admixtures fall into the specialty admixture category and are used to slow down corrosion of reinforcing steel in concrete. In order to protect metallic materials against corrosion, certain inorganic and organic products, called corrosion inhibitors, are added in small concentration to the aggressive medium (Berke, 1989). The addition of corrosion inhibitors to the mix, offers a viable corrosion protection measure (West, 1971; Fontana, 1987). There are generally three groups of inhibitors: anodic, cathodic and mixed inhibitors. Anodic inhibitors reduce the corrosion rate by reacting with the corrosion products and form a protective film. Cathodic inhibitors reduce the corrosion rate by reacting with the cathode sites (as an oxygen-barrier) on the steel. Passivating inhibitors like nitrites represent special types of anodic inhibitors and they are generally very effective if present in sufficient concentrations. Mixed inhibitors both influence the anodic and cathodic reaction sites, by forming an adsorption film on the metal surface. These adsorption type inhibitors are typically organic compounds *e.g.* amines, amino-alcohols, fatty acids (Harrop, 1988; El-Jazairi and Berke, 1990).

Rosenberg and Gaidis (1979) have investigated the inhibition performance of calcium nitrite in simulated concrete pore solution by potentio-dynamic polarisation study and found that calcium nitrite increased the breakdown potential for carbon steel in chloride containing saturated $Ca(OH)_2$ solution. Berke (1986) also presented similar results.

Alonso and Andrade (1983) investigated the inhibition performance of $NaNO_2$ inhibitor in admixed concrete immersed in artificial sea water by applying electrochemical techniques and concluded that $NaNO_2$ inhibitor admixed concrete effectively protects the rebar corrosion, even in less than the optimum content.

Andrade, Alonso and Gonzalez (1986) assessed the effective performance of sodium nitrite inhibitor by electrochemical techniques and found that the effectiveness of the inhibitor was dependent on the chloride-to-nitrite ratio and relative humidity and observed that a nitrite concentration of 3% by weight of cement was generally beneficial.

Hope, Brian and Alan (1989) examined the inhibition effect of $Ca(NO_2)_2$ and $SnCl_2$ on corrosion protection of steel samples submerged in oxygenated lime water containing $CaCl_2$ by electrochemical and visual observation. Under the test conditions, $Ca(NO_2)_2$ appeared to be promising corrosion inhibitor. The nitrite chloride ion threshold level for corrosion was 0.07–0.09. But $SnCl_2$ was found to be ineffective for corrosion protection. Studies by Berke (1989) revealed that the concrete's low permeability prevents the inhibitors from being lost.

Tomosawa *et al.* (1990) investigated the effectiveness of $Ca(NO_2)_2$ as a corrosion inhibitor in chloride containing concrete by two electrochemical methods. In the first method, the chloride and $Ca(NO_2)_2$ had been admixed with reinforced concrete specimen and were subjected to accelerated corrosion by means of alternate drying and wetting. In the second method, reinforced concrete specimens containing $Ca(NO_2)_2$ were repeatedly immersed in chloride solution and dried. These test methods accelerated the penetration of chlorides and the corrosion of embedded steels. From the results of the experiment described above, it was confirmed that the inhibitor prevented the corrosion. Berke, Shen and Sundbeg (1990) determined the appropriate dosage of $Ca(NO_2)_2$ inhibiting admixture by the chloride diffusion curves. They observed that calcium nitrite was found to reduce corrosion on galvanized steel and aluminum reinforcements.

Neagle (1991) studied the mild steel specimens soaked in water or lime water with and without organic corrosion inhibitor (OCI) consisting of mixtures of amines and esters by linear polarization resistance (LPR) and AC-Impedance techniques. The LPR test showed very high resistance for the OCI-treated coupons compared to the reference coupons.

This was confirmed by passive corrosion potential ranged from 198 to -226 *mV vs SCE* compared to –470 to –553 *mV* for the reference. Further FTIR study also revealed the absence of corrosion products (Fe_2O_3 and Fe_3O_4) in the case of OCI.

Dillard (1991) found that the sodium tetra borate inhibitor forms a protective layer on metal surface through the reaction of borate and oxygen, but it directly depends on pH of the pore solution. The test results indicated that borate ions are more mobile in concrete than the chloride ion, indicating an ability to migrate faster to the rebar in concrete.

Sagoe-Crentsil, Yilmaz and Glasser (1993) have found that the water soluble carboxylic acid is an effective inhibitor in presence of 2.5% chloride contamination. A series of laboratory trials (Mackechnie, Rylands and Alexander, 1999) were undertaken to assess the corrosion inhibitor under chloride condition. One mechanistic study of organic based inhibitor revealed that formation of a monomolecular film on both anodic and cathodic sites of the reinforcing steel is responsible for corrosion resistance performance. Therefore, organic type of inhibitors can be classified as a mixed type inhibitor with film forming capabilities.

Berke and Weil (1994) reviewed the performance of inhibitors and revealed that a certain amount of nitrite can stop corrosion up to some level of chloride-ion. Therefore, increased chloride levels require increased levels of nitrite to stop corrosion. They also assessed the inhibition performance of calcium nitrite by electrochemical techniques and the experimental results showed that the typical dosage is of the order of 15 l/m^3 (*i.e.* fifteen *litres* of calcium nitrite admixtures contain 4.14 kg/m^3 of nitrite ion) and further predicted that the steel was protected by the passivating layer of ferric oxide on the surface of steel. A study by Tullumin *et al.* (1995) revealed that the calcium nitrite is an effective corrosion inhibitor. He also investigated cement paste pore solution containing sodium chloride by potentio-dynamic polarization method which indicated passivity break down at a lower potential in the inhibited solution.

Flis and Zakroczymski (1996) studied the inhibition performance of tannin in simulated concrete pore solution (0.6 *M NaOH*, 0.18 *M KOH* and $Ca(OH)_2$) in excess for saturation pH (13.6) along with chloride ions by electrochemical methods and concluded that the tannin slows down the changes in R_{ct} and C_{dl} and found that the protection is due to the film formation of tannin-Fe (III) chelate at the outer surface.

Perez, Moron and Rincen (1997) have investigated the effective inhibition of $Ca_5(PO_4)_3OH$ and $Ca(NO_2)_2$ in 3.5% chloride contaminated concrete by potential-time study and polarization resistance technique for steel corrosion in concrete and observed that $Ca_5(PO_4)_3OH$ showed the same inhibiting effect as $Ca(NO_2)_2$ up to 170 *days*. After 260 *days* none of these inhibitors showed effective protection.

An electrochemical study by Kawamura, Tanikawa and Koto (1997) on the effectiveness of $Ca(NO_2)_2$ and $NaNO_2$ as corrosion inhibitor in chloride contaminated mortar revealed that, Cl^-/NO_2^- ratio in the pore solutions in mortars containing $Ca(NO_2)_2$ were lower than in mortars containing $NaNO_2$ because of the dissipation of greater amounts of Cl^- ions from the pore solutions in the $Ca(NO_2)_2$ than in the $NaNO_2$.

An in-situ photo electrochemical study of inhibitors in chloride contaminated concrete pore solution indicated that the added inhibitor increased the growth rate of passive film even in presence of high chloride content (Wang Shi and Wei, 1998).

A formulation with calcium nitrite as the active ingredient is the most widely used commercial inhibitor for concrete systems in the United States. Calcium nitrite has been proven effective in preventing accelerated corrosion related to chloride contamination of concrete. This inhibitor provides anodic inhibition by raising the valence state of iron in the oxide from +2 to +3 and thus provides a more stable passive film. Although, it has not been shown in concrete, anodic inhibitors typically require a critical concentration to prevent increased localized attack over uninhibited systems. This general property of anodic inhibitors is further complicated by the fact that calcium nitrite is water soluble, thus creating a possible scenario of inhibitor leach out over time and a reduction in concentration to below the critical value. Another problem with calcium nitrite is its toxicity. These shortcomings of calcium nitrite have prompted an investigation to discover new inhibitors worthy of placement in concrete with minimal effects to the structural properties of concrete and also capable of protecting rebar in concrete against chloride attack (Pyc, 1999).

Zhang and Xin (1999) studied the Inhibiting performance of calcium nitrite on rebar corrosion in chloride contaminated concrete by macro-cell study and revealed that the calcium nitrite inhibitor functions by minimizing the anodic reaction and blocking the zone of corrosion. Thus, it makes the half cell potential of rebar in the corrosion process shift to noble. Claude *et al.* (1998) and Pyc (1999) investigated calcium nitrite as an anodic inhibitor and showed that it is ineffective when the chloride to nitrite ratio exceeds approximately 1.0. Further, the inhibitor is water-soluble and therefore, is leachable from the concrete and would become less effective with time. Because the chloride ions will continue to build up in the concrete while the admixed concrete may slowly leach out, eventually the nitrite will not be probably able to inhibit corrosion.

Dhouibi, Triki and Raharinaivo (1999) cautioned about the possibility of accelerated pitting of steel reinforcement in presence of chloride when insufficient nitrite ("Under dosage") is present in concrete. They assessed the inhibition performance of alkanolamine, sodium nitrite and calcium nitrate by electrochemical impedance technique and concluded that the nitrite based inhibitors are generally very effective in protecting rebar corrosion in concrete.

The class of organic inhibitors is typically based on mixtures of alkanolamines and amines (both as additive and migrating compounds) or organic acids (Bdjegovic *et al.*, 1994). The organic inhibitors have been widely applied, since they seem to be effective and their cost is attractive. Kem, and Landolt (2001) suggested that the organic inhibitors provide protection by forming an adsorption layer on the steel surface, hindering steel dissolution.

Napomuceno and De (2000) investigated the inhibition performance of sodium nitrite, amino-alcohol, amines and ammonia based inhibitors in chloride contaminated concrete by polarization resistance technique and revealed that the sodium nitrite inhibitor has the best performance, while the others have a limited efficiency.

Page (2000) assessed the corrosion resistance performance of three inhibitors (calcium nitrite, sodium monofluro phosphate and ethanolamine) on chloride contaminated concrete by electrochemical study and gravimetric analysis and revealed that there was a need for long term field trials with careful control and monitoring.

Wang *et al.* (2000) studied the corrosion inhibition of 1% diethylenetriamine/thiourea (*DETA-TU*) in 0.1 *M/l NaCl* contaminated simulated concrete pore solution under impedance study and stated that *DETA-TU* has double beneficial function for reinforced concrete, *i.e.* densifying the concrete pore structures and adsorbing on the surface of the steel reinforcement.

Dhouibi *et al.* (2000) have investigated the inhibition performance of sodium nitrite and sodium phosphate in saturated $Ca(OH)_2$ as concrete pore solution with chloride contamination and evaluated the mechanistic aspects of inhibitor by DC-polarisation technique through C_{in}/C_{cl} ratio and found that the sodium nitrite is not at all effective, if its concentration is lower than that of the chloride ions but sodium phosphate is totally effective when its concentration equals the chloride concentration.

Monticelli, Frignani and Trabanelli (2000) studied more than 30 compounds as corrosion inhibitors *viz.* alkanolamine, quaternary ammonium derivatives, quarternery phosphonium derivatives BTA and its derivatives, organic acids or their salts, inorganic acids or their salts for concrete application and investigated the inhibitors effectiveness by anodic polarization curves in alkaline chloride solution (saturated calcium hydroxide + $0.1M$ chloride ions) for 30 *days* of exposure period. The inhibitor admixed mortar specimens were assessed by AC-Impedance test. An inhibition efficiency of 88% or 90% after 6 *months* of exposure for chloride polluted mortars was achieved.

Ngala, Page and Page (2002) carried out laboratory investigations to assess the efficacy of calcium nitrite as an inhibitor when used in surface treatments applied to reinforced concrete specimens that were chloride contaminated to varying extents in the presence or absence of carbonation. The corrosion responses of embedded steel bars at various depths of cover were monitored electrochemically during a controlled programme of cyclic wetting and drying undertaken for several months prior to the inhibitor treatment and for approximately 18 *months* thereafter. On completion of the exposure tests, measurements of corrosion weight losses and their distribution on the steel surfaces were also made. In non-carbonated specimens with high levels of internal chloride and carbonated specimens with even low levels of internal chloride, the surface-applied inhibitor treatment appeared to be ineffective under the conditions of the experiments and enhancement of local corrosion rates was observed in some specimens.

Saricimen *et al.* (2002) evaluated the effect of two patented inhibitors on the corrosion of steel reinforcements in concrete using anodic polarization, electron spectroscopy for chemical analysis (ESCA) and Auger electron spectroscopy (AES). The reinforcement corrosion in uncontaminated concrete specimens was evaluated by impressing +4 *V* anodic potential for accelerated corrosion of the steel bar and measuring the time-to-cracking of the concrete specimens. The effectiveness of the inhibitors in retarding reinforcement corrosion in the contaminated concrete specimens was evaluated by measuring the corrosion potentials and corrosion–current density. Results indicated a significant improvement in the corrosion-resisting characteristics of concrete incorporating inhibitors over the control specimens.

Kondratova, Montes and Bermner (2003) investigated reinforced concrete slabs admixed with two commercial corrosion inhibitors calcium nitrite and an organic corrosion inhibitor. The concrete slabs were either un-cracked or pre-cracked. A simulated crack of 0.2 or 0.4 *mm* width was formed transverse to the axis of the reinforcing bar during casting. Slabs were placed about 1 *m* below high tide at the Treat Island, U.S.A. The specimens were visually inspected and the corrosion rates were measured annually using the linear polarization technique. After 3 *years* of exposure, it was found that both corrosion inhibitors were effective in reducing the corrosion rate for un-cracked concrete slabs and the organic inhibitor was more efficient than nitrite in terms of corrosion rate reduction in un-cracked concrete, but both inhibitors were ineffective in the case of pre-cracked concrete slabs.

Singh *et al.* (2003) have studied the effects of hydroxyl ethyl cellulose (*HEC*), oxalic acid and their binary mixtures (1:1, 1:2, 1:3 and 1:4 (by mass of cement)), on the properties of ordinary Portland cement using up to 4% admixtures. They carried out studies on setting time, heat of hydration, strength hardness, fracture toughness and the corrosion resistance tests in H_2SO_4, *HCl* and sea water. They evaluated the corrosion resistance performance by determining the loss in mass of cement mortars. From the setting time experiment, it was found that cellulose acts as a retarder and oxalic acid as an accelerator. The binary mixture (1:3) increased the heat of hydration, strength, hardness, fracture toughness and corrosion resistance. Interaction between components of admixture and various hydrated cementitious phases produced strong bonds, which was expected to give a more durable material as compared to ordinary Portland cement.

Qian and Cusson (2004) investigated the performance of nine commercially available corrosion inhibitors which included concrete admixtures, reinforcing steel coatings and surface coatings on a newly reconstructed barrier wall. On site corrosion surveys, including half-cell potential and corrosion rate measurements, along with concrete coring were conducted on yearly basis, for 5 *years*. The results indicate that the system containing the inorganic-based admixture performed better than the other system in delaying and/or reducing the corrosion of reinforcement in the concrete barrier wall.

Montes, Bermner and Lister (2004) studied the effects of calcium nitrite based corrosion inhibitor (CNI) and crack width, on the corrosion process of the steel reinforcing bars in high performance concrete. Small scale concrete slabs containing reinforcement were cast in concrete with 20 *mm* cover. The slabs were subjected to a simulated marine environment with two cycles of wetting and drying per day over a period of 1 *year*. It was found that CNI alone, in general, has no effect in decreasing corrosion, and that the crack condition of the specimens strongly affects the corrosion process. It was further concluded that the crack width has significant effect on corrosion of reinforcement.

Wombacher, Maeder and Marazzani (2004) reported the behaviour of amino-alcohol based corrosion inhibitors. The interaction mechanism of the inhibitors with steel surface was studied using sophisticated surface analytical methods. It was revealed that the inhibitors delay the onset of corrosion and reduce the rate of corrosion. Apart form their application as concrete admixtures; they can be used as surface-applied-inhibitors on existing concrete structures, in repair mortars or in grouts for rock bolts and anchors.

Nmai (2004) showed the multi-functional benefits of water-based organic corrosion inhibitors in controlling the corrosion of embedded steel and resistance to chemical attack, especially the resistance of concrete to sulphate attack and deterioration due to sulphuric acid exposure. The organic corrosion inhibitor was amines and fatty acid ester based. The corrosion inhibiting performance of this inhibitor was compared with that of calcium nitrite and its effect on mitigating sulphate attack and reducing deterioration due to sulphuric acid exposure, is compared to that of silica fume. It was observed that the inhibitors were effective regardless of concrete quality and significantly reduce the chloride ingress. The permeability reducing property of amine-ester based organic corrosion inhibitor has shown effectiveness in reducing deterioration due to the ingress of other aggressive species such as sulfate and sulphuric acid.

Berke and Hicks (2004) reported the excellent inhibitor property of calcium nitrite. In this study, data were presented that show the levels of chloride at which calcium nitrite will provide the protection. It was further found that once corrosion initiates, the rates are lower with calcium nitrite. An integrated durability model was also suggested.

Vaysburd and Emmons (2004) presented a glimpse of reinforcement corrosion and some of the protection options. The effect of corrosion inhibiting admixtures in concrete and its repair was discussed in detail. It was concluded that as long as one continues to blindly use protection methods applicable for newly constructed structures for concrete repairs, the business of repairing the repairs will be on the rise. A broader understanding of the electrochemical difference between new and repaired concrete is necessary for effective protection of reinforcement in repaired structures.

Gaidis (2004) discussed the chemical reaction of corrosion process in concrete and of the most commonly used inhibitors, with special attention to test procedures and practical issues arising from use of inhibitors. Corrosion inhibition process of calcium nitrite, calcium nitrate and some cathodic inhibitors like amino alcohols, were discussed with the help of chemical reactions.

Murlidharan *et al.* (2004) studied the effect of various inhibitive and complexing ions like hydroxide, citrate and stannate for the corrosion of steel in concrete by weight loss observations, potential-time behaviour, potentio-dynamic polarization and electrochemical impedance studies. It was reported that in 100% *PPC* extracts, the passivity of steel was readily destroyed even in the presence of 10000 *ppm* of chloride. However, in the same environment containing inhibitive and complexing agents like hydroxide, citrate and stannate, the passivity of steel was maintained even in the presence of 30000 *ppm* of chloride.

Trabanelli *et al.* (2005) evaluated the inhibitive action of some organic compounds in controlling the corrosion in carbonated concrete. Electrochemical impedance spectroscopy was used to monitor the corrosion inhibition over a period of 400 *days*. It was concluded that the additives like sodium salts of benzoic acid and particularly 2-amino benzoic acid exhibited some inhibitive effect towards the rebar corrosion process.

Sideris and Savva (2005) investigated the influence of calcium nitrite based corrosion inhibitor on the corrosion of reinforcing steel embedded in 14 different mortars. Two Portland cements, NPC and SR (type I and V according to ASTM Standards) and 12 blended cements were used. The pozzolanic materials used were three lignite fly ashes, silica fume and one natural pozzolana (Milos' Earth). Results showed that calcium nitrite has a beneficial effect in shifting the corrosion potential towards electropositive direction especially in the case of NPC and SR cements. The corrosion potential of blended mixtures was also shifted towards electropositive direction, but since the pozzolanic materials had a beneficial effect by themselves, the reduction was comparative smaller. The beneficial effect of calcium nitrite was also confirmed by the gravimetric weight loss measurements performed after 2 *years* of immersion in the 5% *NaCl* solution.

Blustein *et al.* (2005) reported the inhibitive properties of calcium benzoate for steel corrosion in sodium nitrate solutions at room temperature. Corrosion parameters of the steel/nitrate and steel/benzoate were obtained from polarisation curves. Adsorption parameters of benzoate on steel in sodium nitrate solutions were determined through changes in the degree of surface coverage by the inhibitor, as a function of concentration, time and adsorption potential. The effect of chloride on the corrosion inhibition of benzoate was analysed by exposing the metal in different chloride solution concentrations. The Volta metric profile of steel in calcium benzoate solutions showed little activation by iron dissolution, thus pointing out the inhibitive action of calcium benzoate. The presence of chloride had a deleterious effect on the protective properties of calcium benzoate either on the surface or in solution.

Ann (2006) revealed that the calcium nitrite-based corrosion inhibitor significantly reduced the corrosion rate of steel in chloride contaminated mortar and raised the chloride threshold level, ranging from 0.22% to 1.95% by weight of cement, while nitrite-free specimen produced the threshold level ranging from 0.18% to 0.33%. It was observed that concrete specimens containing the corrosion inhibitor produced the higher total charge passed in a rapid test for chloride ion permeability. An increase in the dosage of corrosion inhibitor resulted in a decrease in the concrete setting time. In addition, the compressive strength at early ages was increased by corrosion inhibitor, but in a long term (900 *days*), decreased to the level for 28 *days*.

Ormellese (2006) investigated the effectiveness of three organic commercial inhibitors in preventing carbon steel chloride induced corrosion in concrete. Three organic compound inhibitor admixtures namely amines-esters, amino-alcohols and alkanolamines were taken; whereas one nitrite based inhibitor was also used for comparison of results. Chlorides were added in concrete mixture from or penetrated from outside by ponding cycles with a 3.5% sodium chloride solution. Solution test and visual examination were carried out over a period of 3 *years*. It was concluded that all the tested inhibitors are able to delay the occurrence of chloride induced corrosion.

Saraswathy and Song (2007) studied the performance of anodic, cathodic mixed inhibitors to control re-bar corrosion in concrete. The anodic inhibitors were sodium nitrite and zinc oxide, whereas, cathodic inhibitors were mono-ethanolamine, di-ethanol amine and tri-ethanol amine. Compressive strength test, tensile strength test, chloride diffusion test and macro cell tests were carried out. It was found that the addition of inhibitors not only controls the re-bar corrosion but also increases the compressive strength of concrete.

In recent years, many investigations and review articles have been published on organic migrating corrosion inhibitor (MCI), which is mainly composed of an amino carboxylate or amino alcohol (Limaye, Angal and Radke, 2000). The inhibitors are either admixtured or directly applied to the concrete surface and it acts under bipolar mechanism which can penetrate even dense concrete by virtue of its vapour pressure and affinity for the embedded steel in concrete. Water based mixtures of amines and esters, supposed by act to form a protective organic layer on the steel bars through chelation process (Nmai, Farrington and Bobrowski, 1992; Bobrowski and Youn, 2000). Studies were carried out to evaluate the anti-corrosion systems in the maintenance, repair and restoration of structures in reinforced concrete using MCIs (Rosignoli, Gelner and Byegovic, 1994). Measurements of corrosion potentials in laboratory tests and on-site monitoring demonstrated the effectiveness of MCI molecules in protecting steel rods from corrosion even in the presence of high concentrations of aggressive salts particularly chlorides. Several investigations were undertaken at tidal zone conditions. It was reported that uncoated concrete shows varying degree of corrosion but normally small at low exposure time which enhances slightly with increasing time.

The dimethyl ethanol amine and triethanol amine based coated rebars in concrete in general show little corrosion (Maeder, 1994; Bdjegovic *et al.*, 1994a; Miksic *et al.*, 1995).

Malik *et al.* (2004) have studied inhibition performance of MCI in protecting steel rods in the presence of high chloride ions in laboratory tests and field exposure. Two types of MCI namely di-methyl ethanol amine and tri-ethanol amine based MCI's were applied as surface coatings. Reinforced concrete specimen coated with these two types of MCI were exposed to 5% *NaCl* solution for lab test and to sea water for field test over a period ranging from 6 to 12 *months*. Apart from visual examination, open circuit potential and polarization tests were also carried out. It was established that the MCI effectively protects the steel rods against corrosion.

Holloway, Nairn and Forsyth (2004) presented inhibitor concentration depth profiles for concrete samples treated with a proprietary migratory corrosion inhibitor (of the Cortec MCI range). The treated concrete was cored and these cores were then sectioned and crushed before being immersed in distilled water to extract the available inhibitor. The amine concentrations were quantified using an ammonium-sensing electrode and were then related to the inhibitor concentration present. The inhibitor examined, was reported to contain a combination of volatile amines and amino carboxylate compounds and was found to readily diffuse through concrete. The inhibitor was subjected to a 5 *year* trial and found to be effective in suppressing corrosion of steel reinforcement in the presence of high chloride concentrations. The concentration profiles indicate that only relatively low concentrations of inhibitor were required to achieve inhibition in this case.

Yongmo, Hailong and Miksic (2004) carried out comparative studies on Cortec MCI-2006 and sodium nitrite in carbonated induced corrosion with and without chloride attack. The corrosion potential and corrosion rate was measured. The results indicate that both corrosion inhibitors can effectively inhibit chloride free, carbonation induced corrosion with minimum dosage (0.8% of MCI and 2% of sodium nitrite). The MCI provides very effective corrosion inhibition at dosage of 1.6% and 2%.

Fedrizzi, Azzolini and Bonora (2005) evaluated the performance of alkanolamine based MCI in concrete specimen exposed to 1-5% chloride ions. Electrochemical techniques, corrosion potential and impedance spectroscopy were used to observe the corrosion behaviour of specimen consisting of concrete and cement mortar.

Mercury intrusion porosimetery was used for the characterization of mortar and total porosity. Chemical analysis was also carried out to determine the amount of chloride penetrated both in mortar layers and in the concrete. It was concluded that the MCI effectively provides barrier protection against rebar corrosion.

2.5 CONCLUDING REMARKS

There is an alarming housing shortage in Asia Pacific region in general and in the Indian context in particular. An economical, simple and durable alternative construction material will contribute greatly in solving the problem of housing. Ferrocement is emerging as a cost-effective, light weight earthquake resistant construction material. It has been established in the earlier sections that ferrocement has performed well under almost all the loading conditions whether it is tension, compression, flexure, shear, torsion, fatigue, impact or the dynamic loading. The material has been increasingly used for both terrestrial and marine environments and competes favorably with reinforced concrete and other building materials. A large number of experimental and analytical studies, which have been reviewed here, deal with ferrocement structural elements, having various shapes and sizes, subjected to different loading conditions. These studies have established the material worthiness for use in diversified applications and prove it to be a strong alternative to conventional construction material. Improvement in strength of ferrocement has also been suggested through the use of different types of wire meshes and modified mortar.

Strength wise, the performance of the ferrocement is extremely satisfactory but the major problem lies with the durability of the material. Success of ferrocement, as with other materials depends largely upon its durability. Reinforcement corrosion is one of the most important criterion governing durability of the ferrocement since the diameter of the wire meshes used in ferrocement are much smaller as compared to the conventional reinforced cement concrete. Protection of reinforcement is usually achieved through the use of galvanized wire mesh. Some researchers have reported the improvement through increase in the effective cover. It has also been suggested that by making dense mortar with the use of additives such as fly ash, silica fumes and blast furnace slag, corrosion of reinforcement can be checked to some extent. The use of appropriate coating over surface of the ferrocement, to control the ingress of corrosive chemicals has also been advised.

These suggested ways have proven to be ineffective with the passage of time, thereby, reducing the strength of the ferrocement components. It has also been reported by various investigators that both galvanized and un-galvanized mesh sustained some degree of corrosion. A study on depth of carbonation showed that CO_2 can penetrate up to a depth of 15 *mm*; where as the usual depth of cover to the reinforcement in ferrocement is 2 to 5 *mm*. Hence the recommendation of enhancing the depth of cover in ferrocement structural component does not appears to be a feasible idea, because on one hand even thick cover could not control the ingress of CO_2, harmful chemical and moisture and on the other hand, an increased thickness of the ferrocement section will be an unwarranted compromise which will also be against the unique feature of material system having high strength to weight ratio.. The idea of preparing an impervious mortar also not seems to be practically possible because the conventional material used in ferrocement are cement and sand, which can not produce an impermeable and impervious mortar, even when well graded sand in used. The use of admixtures like fly ash, silica fume and blast furnace slag though increase the density of ferrocement and reduce the permeability and porosity of mortar matrix but reinforcement in ferrocement even having protection of such mortar, undergoes corrosion especially in aggressive environment. Nevertheless the availability and the cost of these admixtures especially of silica fume are also some un-addressed issues.

Studies undertaken on the chemical reactivity of inhibitors by earlier investigators highlight the worthiness of its application. ACI-549R strongly recommends that studies be undertaken to suggest durable and long term anti corrosion techniques to prevent penetration of water and salts that could lead to the corrosion of reinforcing wire mesh. There is an urgent need to initiate detailed investigations incorporating various methodologies and techniques for reducing the corrosion in ferrocement. Use of chemical corrosion inhibitor in ferrocement is rarely sighted in literature. Only a few studies are reported which deal with the chemicals like chromium trioxide to address a particular problem of galvanic cell, a patented admixture and a polymer-modified coating to control the reinforcement corrosion. User friendly, easily available and cost effective chemical corrosion inhibitors for ferrocement have not been identified in literature. The dose of corrosion inhibitors and its effective application techniques have not been addressed. The adverse effect on setting time of cement, compressive and tensile strength of cement-sand mortar has also not been given due attention.

Studies undertaken earlier clearly reveal that many inorganic and inorganic compounds are potential corrosion inhibitors. Calcium nitrite, calcium nitrate, potassium dichromate, stannous chloride, lead chromate, sodium nitrite, sodium benzoate, ethyl aniline, mercaptobenzothiazole, ethamolamine, zinc chromate, calcium hypophosphite, methyl ethanolamine, sodium thelate, calcium stearate and tannin are among a few of these. Use of migratory corrosion inhibitor compounds based on amino carboxylate, amino alcohol, dimethyl ethanol amine and triethanol amine including some patented compounds are also reported in literature. However some inhibitors are effective, while others have problems with some of the concrete properties. Limited information is available on actual field performance and cost-effectiveness. Many aspects such as the effect of chemical inhibitors on the setting time, compressive and tensile strength of cement; pH value; appropriate dose for different kind of environment, effective application technique, and long term behaviour continue to be partially explored only. Comprehensive recommendations for the utilization in day to day construction practice are still awaited.

It can be fairly concluded that a wide scope is left to undertake investigations aimed at improving the durability of ferrocement through use of corrosion inhibitors addressing the issues that will have a bearing on it's effectiveness to delay/seize the corrosion of reinforcement in ferrocement without any adverse effect on it's long term behaviour.

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Chapter 3

Reinforcement Corrosion Mechanism and Control

3.1 GENERAL

The corrosion process of metal reinforcement within ferrocement elements are basically similar to those associated with steel reinforcement in conventional reinforced concrete. In this chapter an attempt has been made to review the mechanism, monitoring techniques and control of reinforcement corrosion in general cementitious composite which of course includes both reinforced concrete and ferrocement.

As per the updated corrosion map of India (Fig. 3.1), drawn by Central Electrochemical Research Institute Karaikudi, Tamil Nadu, India, (CECRI, 2004), Sriharikota on the Andhra Pradesh coast is first most corrosion prone place in India. Chennai stands second, thanks to its ever increasing vehicle pollution and proximity to the sea, it has rendered the city's buildings structurally less stable than they seem. The annual loss due to corrosion can be compared with that of other natural calamities like earthquake and cyclone, only its impact is indirect. Loss due to corrosion has been reported to account for more failure in terms of cost and tonnage than any other environment. The overall loss due to corrosion alone amounts to at least 2%–4% of GNP and at least 25%–50% of this could be avoided by using appropriate corrosion control technology. Apart from its direct costs, corrosion is a serious problem, because it definitely contributes to the depletion of our natural resources. Although corrosion is inevitable, it can be considerably reduced.

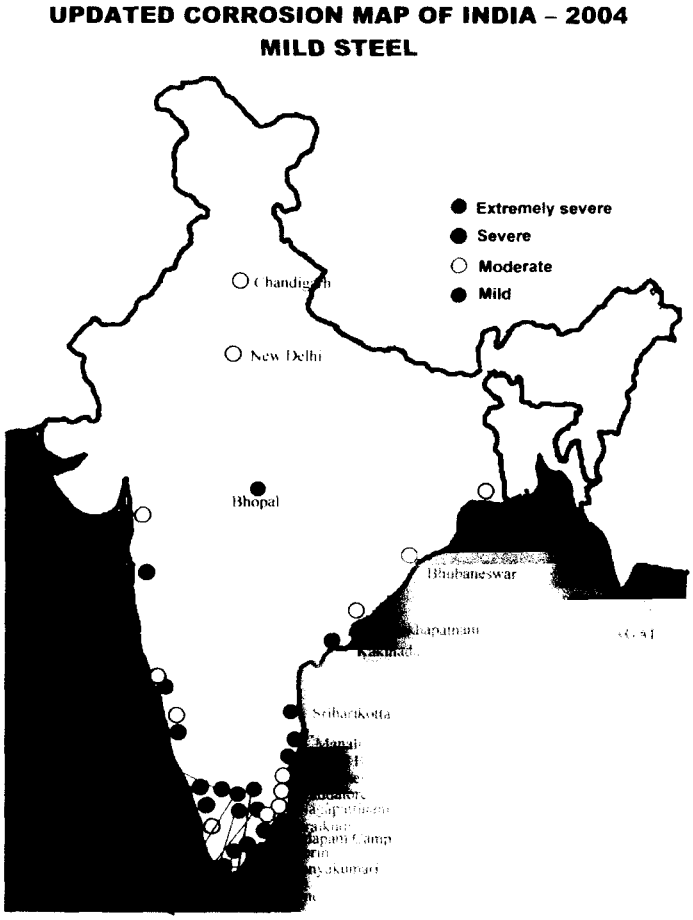

Fig. 3.1 Updated Corrosion Map of India for Mild Steel, 2004

In India alone, about 700 bridges especially in coastal regions are under distress. The 740 *m* long Princess street fly over in Mumbai, India, located very near to the sea, was badly cracked within 9 *years* of it's commissioning due to saline environment. A reinforced concrete pier at Trivendram, India extending 72.75 *m* into the sea suffered deterioration within 7 *years* of it's construction. The highway research station, Madras surveyed 80 concrete bridges along the coast of Tamil Nadu and brought out many instances of spalling and cracking together with extensive corrosion of reinforcement.

In United States, majority of the structures exposed to even mildly aggressive environment showed evidence of deterioration within 10 *years*. In the Union of South Africa, it has been observed that reinforced concrete structures exposed to marine atmosphere deteriorate in relatively shorter period. According to an estimate the annual cost of corrosion in United States of America (U.S.A.) and Australia is around $126 *billion* and $2.5 *billion* respectively. In U.S.A. alone, the cost of repairing and replacing structures deteriorated by corrosion is estimated to be more than $20 *billion* and is said to be increasing at a rate of $500 *million per year* (Jamil, 2005).

Concrete is primarily a construction material and offer barrier protection to steel rebar even under aggressive conditions. In general, concrete is providing a passivating protective coating for rebars. It is a fact that the high alkalinity and fairly high electrical resistance of concrete can very effectively protect the steel rebar under all conditions. However with the passage of time, in real exposure condition, it is very difficult to maintain these basic requirements of concrete. Constituents of the cementitious composite can be broadly divided into two parts namely the matrix which includes cement and aggregate; and the reinforcement. The reduction in the durability of composite can be attributed to the deterioration of matrix as well as of the reinforcement.

3.2 FACTORS RESPONSIBLE FOR MATRIX DETERIORATION

The factors primarily responsible for the deterioration of matrix during the prolonged exposure are:

(i) Carbonation

(ii) Sulphate attack

(iii) Reduction in alkalinity by leaching action and reaction with matrix.

3.2.1 CARBONATION

Carbonation of concrete is a process by which carbon dioxide in the ambient air penetrates the concrete and reacts with the hydroxides, such as calcium hydroxide, to form carbonates. Carbonation and rapid drying of fresh concrete may affect surface durability, but this is prevented by proper curing. Carbonation of hardened concrete does not harm the concrete mixture. However, carbonation significantly lowers the alkalinity (pH) of the concrete. High alkalinity is needed to protect embedded steel from corrosion; consequently, concrete should be resistant to carbonation to prevent steel corrosion.

Fresh concrete or similar cementitious composite like ferrocement has a pH value around 12.5. The moist carbon dioxide present in the atmosphere reacts with the alkaline material present in composite as,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \qquad (\text{pH} = 7) \qquad (3.1)$$

This neutralization is a continuous process. Hence the pH value near the rebar drops to 8-9, which leads to the corrosion of rebar with the formation of different complex iron oxides. Moreover, the carbonated matrix does not have the same capacity for binding chloride as does non-carbonated matrix which increase the free chloride content in matrix (Burge, 1983).

3.2.2 SULPHATE ATTACK

Sulphate attack has long been recognised as an important reason for concrete deterioration in a wide variety of structures. Sulphate attack in concrete has been known to occur when sulphate solutions, derived either from a constituent in the concrete such as aggregate or from external sources such as groundwater, react with the calcium aluminate hydrates present in the hardened cement to form the gypsum and the hydrated calcium sulfoaluminate known as ettringite.

It is caused by the following chemical reactions between concrete and sulphate,

$$Ca(OH)_2 + Na_2SO_4.10H_2O = CaSO_4.2H_2O + 2NaOH + 8H_2O \quad (3.2)$$

$$4CaO.Al_2O_3.19H_2O + 3CaSO_4.2H_2O + 16H_2O = 3CaO.Al_2O_3.3CaSO_4.31H_2O + Ca(OH)_2 \quad (3.3)$$

$$3CaO.2SiO_2 + 3MgSO_4.7H_2O = CaSO_4.2H_2O + 3Mg(OH)_2 + 2SiO_2 \quad (3.4)$$

Thus the conversion of $Ca(OH)_2$ and calcium aluminate to gypsum and ettringite more than doubles the solid volume, inducing cracks in concrete structure. These reactions can inflict serious damage on concrete, leading to weakening and perhaps ultimate failure of the affected structure (Lea, 1971).

3.2.3 REDUCTION IN ALKALINITY BY LEACHING ACTION AND REACTION WITH MATRIX

For structures completely submerged in water, the leaching of lime is a major weakening factor. During leaching process, hydroxide ion is always diffused outwards. If excessive leaching of lime takes place, it will increase the porosity and decrease the strength and durability of structures. The presence of chemicals like ammonium chloride, ammonium sulphate and acids like hydrochloric acid, sulphuric acid, phosphoric acid *etc.*, in the environment bring about accelerated deterioration of the concrete (Burge, 1983).

3.3 FACTORS AFFECTING REINFORCEMENT CORROSION

Reinforcement corrosion in concrete is mainly caused by the following factors:

(i) Non-homogeneity of the matrix

(ii) Applied stress

(iii) Depassivation of reinforcement by chloride ions.

3.3.1 NON-HOMOGENEITY OF THE MATRIX

One of the major factors in influencing rebar corrosion is the inherent heterogeneity of the matrix. Steel in concrete with contaminated ingredient of concrete becomes anodic (contacts with chloride, oxygen and water) as compared to that of uncontaminated concrete, initiating active rebar corrosion.

3.3.2 APPLIED STRESS

Concrete structures have to perform under a variety of complex environmental conditions. Bridge structures have to function under dynamic loading condition in aggressive environments where safety and durability are of paramount importance. These environments favour corrosion cracking of steel. It is generally known that the high strength steel is susceptible to stress corrosion cracking in a variety of environments (Carter, Hayat and Cotton, 1972). Particularly steel with bainitic structure are more susceptible than those with pearlitic or sorbitic structure. Oil tempered wires fail much more easily under stress corrosion than do hard drawn stress relieved wires. Stress corrosion failures, during service, have occurred particularly in sulphite, nitrate and chloride environments (Talbot and Talbot, 1998; Newman, 2002).

3.3.3 DEPASSIVATION OF REINFORCEMENT BY CHLORIDE IONS

Of the various anions encountered in corrosive environments, chloride has acquired a significant reputation as the most aggressive ion. Earlier study revealed that chloride ions have high penetrating power in the passive oxide films on metals. This effect is considered to be associated with its smaller size in comparison to other ions.

In reinforced concrete structures, the pore solution surrounding the reinforcement attains a pH of around 12.5 after the completion of hydration reaction. The alkalinity is buffered at this pH by calcium hydroxide in a lime rich layer in intimate contact with the surface of the reinforcement. As long as the pH remains in the passive region, the rebar also remains free from corrosion (Leek and Poole, 1990). The most common cause of rebar corrosion problem stems from the introduction of chloride ions. The contamination of the chloride in concrete structures by chloride occurs due to (i) their use as accelerator in the mix, (ii) by the presence of a marine atmosphere and, (iii) the use of deicing salts. Chloride occurs in concrete in three forms namely chemically bound, physically adsorbed and frees chlorides (Tutti, 1982).

Among all, only the free chlorides are mainly responsible for rebar corrosion. If the free chloride to hydroxide ratio exceeds 0.6, loss of passivity occurs and pitting progresses. The free chloride not only alters the Porbaix equilibrium diagram (Fig. 3.2), it reduces the area of passive region, but also transfers the rebar from the passive to the active region (El-Sayed, 1986; Chalisgaonkar, 1987).

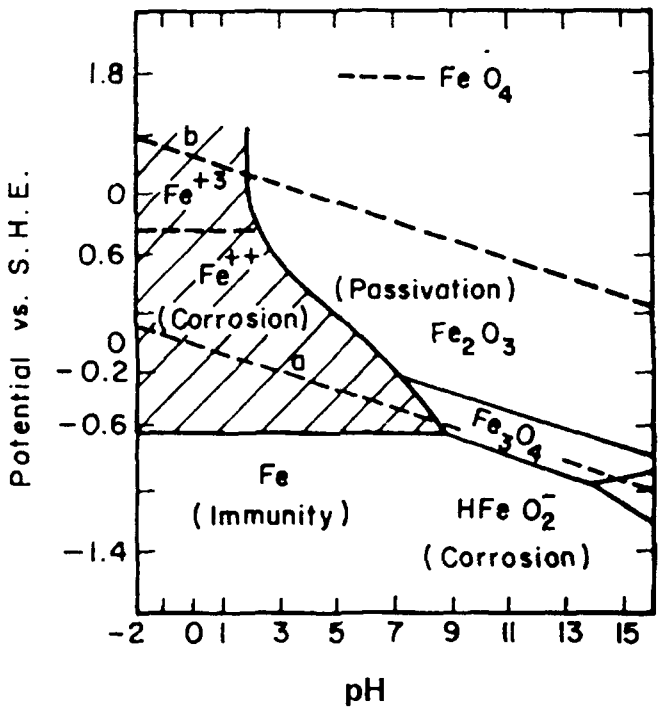

Fig. 3.2 Pourbaix Diagram for the Iron-Water System at 25°C Showing Nominal Zone of Immunity, Passivity and Corrosion (Chalisgaonkar, 1987)

The corrosion reaction that occurs can be represented as given below (Erlin and Verbeck, 1978; Leygraf, 2002):

$$Fe = Fe^{2+} + 2e^{-} \tag{3.5}$$

$$O_2 + 2H_2O + 4e^{-} = 4OH^{-} \tag{3.6}$$

$$Fe^{2+} + 2OH^{-} = Fe(OH)_2 \quad \text{(White corrosion product)} \tag{3.7}$$

$$4Fe(OH)_2 + 2H_2O + O_2 = 4Fe(OH)_3 \quad \text{(Red Rust)} \tag{3.8}$$

$$3Fe + 8OH^{-} = Fe_3O_4 + 4H_2O + 8e^{-} \quad \text{(Black Rust)} \tag{3.9}$$

At high chloride concentrations,

$$Fe + 2Cl^{-} = FeCl_2 = Fe^{2+} + 2Cl^{-} + 2e^{-} \quad \text{(Yellowish Green)} \tag{3.10}$$

$$6FeCl_2 + O_2 + 6H_2O = 2Fe_3O_4 + 12H^{+} + 12Cl^{-} \tag{3.11}$$

The iron-free chloride reaction is self-perpetuating in the sense that, the free chloride originally responsible for the reaction is released for reuse, when iron hydroxide is formed, as shown Fig. 3.3. In fact, the free chloride acts as a reaction catalyst. Even though a high level of alkalinity remains around the steel embedded in concrete, the chloride ions can locally depassivate the steel and promote rebar corrosion problem. Usually concrete and steel do not deteriorate at same rate. The reason for this is the conditions leading to the deterioration of the concrete do not necessarily corrode the steel and vice-versa. It is true however, that the deterioration of the concrete usually accelerates the corrosion of the steel rebars and vice-versa (Fraczek, 1987).

3.4 MONITORING METHODS FOR MATRIX DETERIORATION

Corrosion monitoring is defined as the systematic measurement of corrosion rate for examining the health of the structures and equipments periodically. The in-situ corrosion monitoring techniques provide information on the state of condition of reinforcement bars and concretes in the case of concrete structures. They also correlate the corrosion process with the concrete variables. The losses due to reinforcement corrosion run into several *millions* of *rupees* due to reduced life of reinforcements.

So measurement of the extent of deterioration of concrete and the corrosion rate of rebar are very essential for adopting suitable preventive measures of structures at the right time.

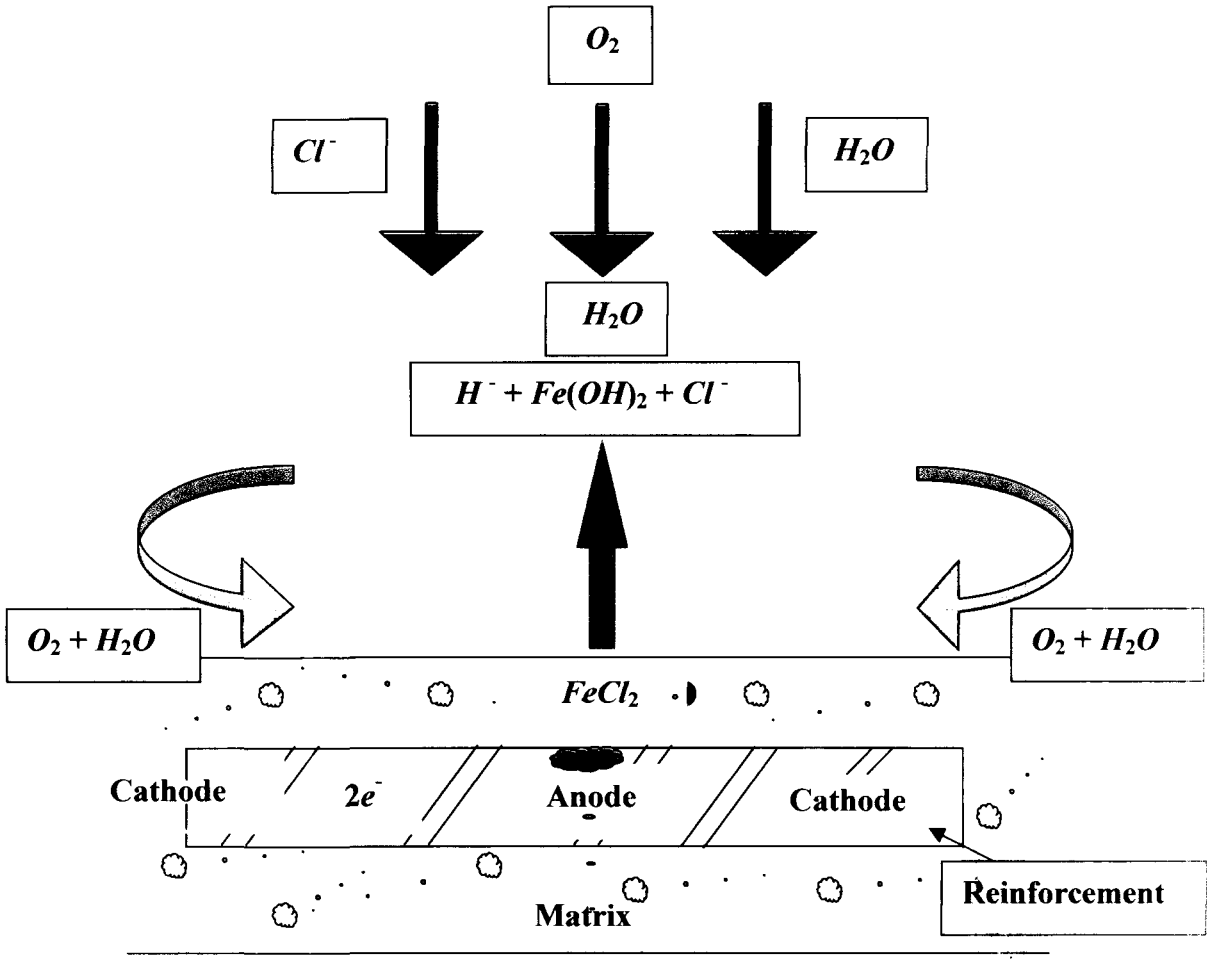

Fig. 3.3 Corrosion Process for Steel in Cementitious Composite

3.4.1 TECHNIQUES FOR MONITORING MATRIX DETERIORATION

Cementitious matrix contains substances such as CaO, Na_2O and K_2O which provide an alkaline environment. As the concrete is highly alkaline in nature, the acidic materials present in the atmosphere like SO_2, H_2S and CO_2 easily attack the concrete structures and cause deterioration.

Field inspection and visual observation directly indicate the following defects in the deteriorated concrete structures (Browne, Goghegan and Bater, 1983; Manning and Bye, 1983; FIP, 1986; ACI-201-1R, 1997):

(i) Scaling

(ii) Efflorescence

(iii) Rust stains

(iv) Incrustation

(v) Pop-outs

(vi) Dampness

(vii) Discolouration

(viii) Honey combing and air pockets

(ix) Longitudinal, transverse, diagonal and random cracks.

Insitu strength determination is used for finding out the deteriorated areas. Core sample analysis for strength, alkalinity, free chloride and free sulphate tests are common. If the free chloride and the fee sulphate content exceed the threshold value then the corrosion at the rebars is quite possible. The tolerable limit for chloride is 0.1% by weight of the concrete (Rengaswamy *et al.*, 1987). On the basis of survey made on concrete structures in Britain, the BRE (Holden, Page and Short, 1983) proposed the following classification for assessing the risk of the corrosion in terms of acid soluble chloride contents by weight of cement:

Low Risk	Medium Risk	High Risk
< 0.4%	0.4 – 1%	> 1%

When struck with suitable hammer, the areas which give off a hollow sound indicate the dummy areas in the existing concrete structures.

3.4.2 IDENTIFICATION OF CARBONATED CONCRETE

In the existing structures, the carbonated portions are identified using Bromo-cresol purple indicator or with phenolphthalein indicator. The Bromo-cresol indicator when sprayed on existing concrete structures produces a yellow colour in carbonated areas and a violet colour in non-carbonated areas. The phenolphthalein indicator when sprayed on the existing concrete structure produces a purple colour on the un-carbonated areas, while the carbonated areas remain colourless (Rengaswamy *et al.*, 1987).

3.4.3 IDENTIFICATION OF ALKALI-SILICA REACTIVITY

To identify the alkali silica reaction in the existing concrete structures, a 5% solution of uranyl acetate is applied on the concrete surface and allowed to react for about 5 *minutes*. An ultraviolet light is then made incident on it. If the alkali-silica reactivity is present, it will reveal a greenish yellow glow (NRC Hand Book, 1991).

3.4.4 IDENTIFICATION OF SULPHATE ATTACK ON CONCRETE STRUCTURES

For the identification of sulphate attack on concrete structures some quinalizarin regent is sprayed on the existing concrete structures. The sulphate attacked portions become crimson in colour in contact with gypsum (Poole and Thomas, 1975).

3.4.5 NON DESTRUCTIVE TESTING TECHNIQUE

The popularly used non-destructive testing techniques to asses the concrete deterioration are:

(i) Resistivity measurement using four probe resistivity meter

(ii) Ultrasonic pulse velocity technique

(iii) Radiography technique

(iv) Infrared thermography technique

3.4.5.1 RESISTIVITY MEASUREMENT

The method essentially consists of using a four probe technique in which a known current is applied between two outer probes and the voltage drop between the inner two elements is measured in terms of resistance (R). The equation relating resistivity to measured resistance has been derived from the four probe method.

Resistivty of concrete $\rho = 2 \pi a R$ (3.12)

where, a = inter electrode distance in *cm*; R = measured resistance in *ohm*.

The factors which govern the resistivity values are:

(a) Constituents of concrete

(b) Chemical contents of concrete such as moisture, chloride level and other ions regardless of whether or not these were introduced by formulation, atmospheric or sea water penetration.

(c) Type of pore structure of concrete.

It is possible that resistivity values will vary quite significantly over a structure. The values given in Table- 3.1 indicate the general guidelines of resistivity values based on which the probable corrosion risk can be identified in concrete structures (Selveraj, 2007).

Table- 3.1 Relationship between Resistivity and Corrosion Probability

S. No.	Resistivity (Ω *cm*)	Corrosion Probability
1.	Greater than 20,000	Negligible
2.	10,000–20,000	Low
3.	5,000–10,000	High
4.	Less than 5,000	Very High

3.4.5.2 ULTRASONIC PULSE VELOCITY TECHNIQUE

This technique is more helpful in locating the defects and cracks in concrete structures. The interpretation of data is very difficult as a large number of factors affect the pulse velocity (ASTM C-597, 2002). The relationship between the pulse velocity and the quality of concrete is given as below in Table- 3.2.

Table- 3.2 Relationship between Pulse Velocity and Quality of Concrete

S. No.	Longitudinal Pulse Velocity (*km/sec*)	Approximate Compressive Strength (N/mm^2)	Quality of Concrete
1.	Below 2.0	---	Very Poor
2.	2.0 – 3.0	4.0	Poor
3.	3.0 – 3.5	Up to 10	Fairly Good
4.	3.5 – 4.0	Up to 25	Good
5.	4.0 – 4.5	Up to 40	Very Good
6.	Above 4.5	Above 40	Excellent

3.4.5.3 RADIOGRAPHY

The use of Gamma and X-rays has been widely reported in literature. Gamma ray transmission has been used to measure the thickness of the concrete slab. Voids in concrete as small as 5 *mm* in 130 *mm* thick beams have been detected, using gamma rays. Arrangements of aggregate particles, air voids, paste film thickness, segregation and location of cracks have been evaluated in concrete using X-rays. These have also been used to detect the amount of corrosion of rebar in chloride contaminated concretes and to evaluate corrosion products on rebar embedded in concrete. Defects in post-tensioned concrete beams were studied using X-rays and gamma rays. The Swath ling bridge, Southampton, U.K., was investigated using high energy X-rays to assess radiation hazards and establish the usefulness of this technique for in-situ examination of reinforced concrete structures (Priess, 1966; Manning, 1988). The quality of concrete can be assessed using the values given in Table- 3.3.

Table- 3.3 Relationship between Scatter Reading and Quality of Concrete

S. No.	Back Scatter Reading (*mm*)	Density (kN/m^3)	Concrete Quality
1.	8.5	> 23.0	Good
2.	7.5–8.5	23.0–20.0	Below average
3.	7.5	< 20.0	Poor

Central Electrochemical Research Institute (CECRI), Karaikudi, Tamil Nadu, India. has made use of high energy (6 *MeV*) Betatron radiographic equipment for carrying out the condition survey of concrete bridges especially in girders and beams. For the first time in India, radiographic examination of one of the bridge has been carried out by CECRI (Rengaswamy, 1993). The study gave information on the quality of the concrete, grouted and ungrouted portions, tensioned and un-tensioned steel.

3.4.5.4 INFRARED THERMOGRAPHY TECHNIQUE

The application of infrared thermography has provided a reliable and accurate assessment method for the inspection of buildings and structures. The principle of the infrared thermography technique is the detection of energy by an infrared scanner and mapping the temperature contours over the surface of a target object to provide an appropriate measure of the damaged building or structure.

This technique identifies the areas of delamination in existing concrete structures. Delamination occurs due to corrosion of reinforcing steel embedded in concrete or due to poor bond between two-course placements (Buyukozturk, 1998; Lo and Choi, 2004).

3.5 TECHNIQUES FOR MONITORING CORROSION OF REINFORCEMENT

As the corrosion process is an electrochemical phenomenon, electrochemical techniques have been found to be useful for studying corrosion of rebars in concrete structures. The advantage of electrochemical techniques is their simplicity and quickness. They can be easily implemented both in laboratory and field conditions.

Some of the common techniques used for the monitoring reinforcement corrosion are given below:

(i) Gravimetric weight loss method.
(ii) Open circuit potential (OCP) measurements
(iii) Surface potential (SP) measurements
(iv) Polarisation resistance method
(v) Impedance technique
(vi) Harmonic analysis
(vii) Noise analysis

3.5.1 GRAVIMETRIC WEIGHT LOSS METHOD

A comprehensive guideline for the preparation of specimens for gravimetric method is given in ASTM G1 (2003). Weighed metal specimen (W_i) is exposed for a specified period. At the end of the exposure period, the rebar specimen are removed from concrete, cleaned in Clarke's solution and weighed again (W_f). The difference between the two weights ($W_i - W_f$) will give the actual loss of metal (W).

The metric expressions for uniform corrosion penetration are *micrometers* (*microns* or *μm*) *per year* for most corrosion rates although *millimeters per year* (*mmpy*) may be required for rapid corrosion rates.

Mils i.e. *thousandths of an inch, per year* (*mpy*) is the most desirable way of expressing corrosion rates (Fontana, 1987). The corrosion rate is calculated from weight loss data using the Eqns. 3.13 and 3.14.

$$\text{Corrosion Rate in } (mpy) = \frac{534 \times W}{D \times A \times T} \tag{3.13}$$

$$\text{Corrosion Rate in } (mmpy) = \frac{87.6 \times W}{D \times A \times T} \tag{3.14}$$

where, W = weight loss of the specimen in *mg*

D = density of the specimen in gm/cm^3

A = surface area of the specimen in *sq. inch* for Eqn. 3.13 and in cm^2 for Eqn. 3.14

T = exposure time in *hours*

3.5.2 OPEN CIRCUIT POTENTIAL MEASUREMENTS

The tendency of the metal to react with an environment is indicated by the potential it develops on contact with that environment. In reinforced concrete structures, concrete acts as an electrolyte and the reinforcement will develop a potential depending on the nature of the concrete environment which may vary from place to place. The electric circuit for open circuit potential measurements is given in ASTM C-876 (1998). As per this code, probability of reinforcement corrosion is given as below (Table- 3.4).

Table- 3.4 Relationship between OCP and Probability of Corrosion

S. No.	Open Circuit Potential (OCP)		Probability of Corrosion
	*mV vs SCE**	*mV vs CSE***	
1.	More (–)ve than –275	More (–)ve than –350	> 90%
2.	Between –275 to –125	Between –350 to –200	Uncertain
3.	More (+)ve than –125	More (+)ve than –200	< 10%

* Saturated Calomel Electrode

** Copper/Copper Sulphate Electrode

3.5.3 SURFACE POTENTIAL MEASUREMENTS

During corrosion process, electric current flows between the cathodic and anodic sites through the concrete. This flow can be detected by measurement of potential drop in the concrete. Hence, surface potential measurement is used as a non-destructive testing for identifying anodic and cathodic regions in concrete structures and indirectly detecting the probability of corrosion of rebars in concrete. Electrical connection to the rebar is not necessary in this technique (ASTM C-876, 1998).

3.5.4 POLARISATION RESISTANCE TECHNIQUE

Among the various electrochemical techniques, the best known technique for evaluation of instantaneous corrosion rate in the laboratory is the polarization resistance method. This technique was developed by Stern and Geary (1957). The principle involved in this technique is that a linear relationship exists between potential and applied current. Based on the kinetics of electrochemical reactions and the concept of mixed potential theory postulated by Wagner and Traud an equation was derived, which relates quantitatively the slope of the polarization curve in the vicinity of the corrosion potential to the corrosion current density (I_{corr}) as given by Eqn. 3.15.

$$I_{corr} = \frac{b_a \times b_c}{2.303(b_a + b_c)} \times \frac{1}{R_p} \tag{3.15}$$

where, b_a = Anodic Tafel slope

b_c = Cathodic Tafel slope

$R_p = \frac{\Delta E}{\Delta I}$ = Polarization resistance

This principle can be applied to estimate the corrosion rate of rebars embedded in concrete. In this technique a small amount of D.C. current (ΔI) is applied to the embedded rebar and the corresponding potential (ΔE) is monitored. This polarization can be carried out for a specified potential in the vicinity of open circuit potential (OCP). There are three methods to carryout the polarization measurements:

(i) Galvanostatic method

(ii) Potentiostatic method

(iii) Potentiodynamic method

In the galvanostatic method, a small increment of current is applied and the change in potential is monitored. For each increment of current a waiting time of 10 *minutes* is necessary in order to obtain corresponding stabilized E values. In the potentiostatic method, for each increment of potential (ΔE), the current value (ΔI) is recorded after 30–60 *seconds*. In the potentio-dynamic method, the potentiostat is coupled with a voltage scan generator and the polarization is carried out at a particular sweep rate. Reliable results have been obtained for lower scan rates. Polarisation can be carried out by any one of the above methods and E *vs* I plot can be obtained. From this plot, R_p value can be calculated. Usually the value of Tafel slope b lies between 13 and 52 mV depending on the passive and active corroding condition.

3.5.5 IMPEDANCE TECHNIQUE

In recent years, A.C. impedance spectroscopy is being experimented as a useful non destructive technique for quantifying corrosion of steel rebars embedded in concrete (Fontana, 1987). Impedance (Z) is the ratio of A.C. voltage to A.C. current. An alternating voltage of about 10 to 20 mV is applied to the rebar and the resultant current and phase angle are measured for various frequencies. As per the circuit, cell impedance is expressed by Eqn. 3.16.

$$|z| = R_s + \frac{R_t}{1 + J\omega C_{dl} R_{ct}} \tag{3.16}$$

where, $\omega = 2\pi f$

$J = \sqrt{-1}$

R_s = Resistance of concrete

C_{dl} = Double layer capacitance

R_{ct} = Charge transfer resistance

As $\omega \longrightarrow 0$, the cell impedance $|z| = R_s + R_{ct}$ and as $\omega \longrightarrow \infty$, the cell impedance $Z = R_s$, hence subtraction of cell impedance Z at high frequency from that at low frequency gives R_{ct}. Corrosion current, I_{corr} can be calculated from R_{ct} using well known Stern-Geary equation (Eqn. 3.15).

3.5.6 HARMONIC ANALYSIS

The harmonic analysis method is an extension of impedance method. It is relatively new technique, that is quicker to carry out and leads to results which are easy to understand than those of the electrochemical impedance method. A simple amplitude sinusoidal voltage of 10 mV is applied to perturbate the working electrode in the same manner as the electrochemical impedance method. However only a single frequency is employed and the current response is measured in terms of the fundamental, first and second harmonics. This technique is quick and the advantage over other electrochemical techniques is that it enables the calculation of the Tafel slopes directly from the system under test. However this technique is still in an experimental stage.

3.5.7 ELECTROCHEMICAL NOISE ANALYSIS

Electrochemical noise technique is an emerging technique for monitoring corrosion of reinforced concrete structures. This technique enables information on the mechanism and rate of corrosion processes at areas identified in concrete structures. A low amplitude variation of the corrosion potential of steel in concrete is measured to obtain a noise data as a record of potential fluctuations in the form of power spectra. A noise source is located within the probable corroding area, and time record of sufficient interval is monitored over the frequency range (10 μHz to 1 Hz). Noise data as a record of potential fluctuation is obtained. The noise signal is transformed from time domain to frequency domain displayed in the form of amplitude and frequency based on either fast transform or maximum entropy method of spectral analysis. This measurement interval is usually between 2–20 *seconds* depending upon frequency range (Aballe, Bethencourt and Marcos, 1999; Roberge, 1999; Eden, 2000).

3.6 CORROSION PROTECTION METHODS

Detailed analysis of factors which influence corrosion mechanisms and process, indicate that corrosion protection requires a multiple approach. There are many possible approaches as listed below:

(i) Coating of reinforcement

(ii) Galvanized reinforcement

(iii) Using stainless steel bars

(iv) Coating to concrete surface

(v) Using chemical admixtures

(vi) Cathodic protection

(vii) Electrochemical removal of chloride

(viii) Re-alkalization

(ix) Using blended cement

(x) Using chemical corrosion inhibitors

3.6.1 COATING TO REINFORCEMENT

This is an effective means of controlling corrosion in such environment where ordinary concrete with surface coating is not able to protect the reinforcement against corrosion. There are several methods of providing protective coatings to the reinforcement. The prevalent coatings used are inhibited and sealed cement slurry coating, cement polymer composite coating and epoxy coating (Babaei, Khossrow and Hawkins, 1988; de Wit, Weijde and Ferrari, 2002).

3.6.2 GALVANISED REINFORCEMENT

Galvanised reinforcement consists of standard black bar, hot dipped in molten zinc (Anon., 1996; Belleze *et al.*, 2006). This process forms a coating which is metallurgically bonded to the surface of the parent metal. The surface of the zinc reacts with calcium hydroxide in the concrete to form a passive layer, preventing corrosion. It has been used in bridges and similar high value structures for the last 20 *years* or so in the United States and parts of Europe and in some buildings in India.

3.6.3 STAINLESS STEEL REINFORCEMENT

Stainless steel is the name given to a family of corrosion resistant steel containing a minimum of 12% chromium. On contact with air, chromium forms a thin oxide layer on the surface of steel, this is passive and resists corrosion. The addition of other elements such as nickel and molybdenum enhances the passivity and thus improves the corrosion resistance. As the oxide layer is formed by the elements in the stainless steel rather than being an applied coating, it is in fact self-repairing. Thus, if the damage does occur during handling and fixing, the passive oxide layer rapidly re-forms and the corrosion resistance is not affected (Srensen, Jensen and Maahn, 1990; Blanco, Bautista and Takenouti, 2006).

3.6.4 COATING TO CONCRETE SURFACE

Concrete is permeable to water and solutions of chloride and sulphates. The penetration of aggressive salts accelerates rebar corrosion and failure of concrete structures. In order to prevent the penetration of aggressive salts, the concrete coating must serve as an effective barrier against ingress of salts, gases and moisture. Types of coating normally used are based on silicates, latexes, acrylics, siloxanes, chlorinated rubber, polyvinyl chloride etc. (Babaei, Khossrow and Hawkins, 1988; Anon., 1996).

3.6.5 USING CHEMICAL ADMIXTURES

The chemical admixtures modify the properties of hardened concrete. Most admixtures are supplied in ready to use liquid form. The effectiveness of an admixture depends on various factors including: type of cement used, water-content, mixing time, slump, temperature of the concrete and air content of concrete. Chemical admixtures can be classified according to their function. There are five distinct classes of chemical admixtures. Examples are water reducing, retarding, accelerating, plasticising (superplasticising) and air entraining admixtures. All other varieties of admixtures fall into the speciality category whose functions include corrosion inhibition, shrinkage reduction and alkali-silica reactivity reduction *etc.* Some of the chemical admixtures used for application in reinforced concrete are mentioned in the literature. A vast majority of them have been subjected to screening studies in aqueous simulated pore solution with only a few added as an admixture to concrete. Among them are: barium and potassium chromate, calcium and silicon fluorides, sodium benzoate, metasilicate, sodium nitrite, aluminum acetate, chromic oxide, thiourea, barium metoborate, sodium phosphate, sodium molybdate, sodium silicate, potassium nitrate, zinc borate (Craig and Wood, 1970; Taylor *et al.*, 1996), Alkalis, tetramethyl and tetrabutyl quaternary ammonium salts (Hettiarachchi, Gaynor and Asaro, 1990; Hettiarachchi and Gaynor, 1992), Butyl ester emulsion and dimethyl ethanolamine (DMEA), Formaldehyde and Water-soluble mono- and di-carboxylic acids (Whiting, 1978; Lotto, 1992; Sagoe-Cretsil, Yilmaz and Glasser, 1993; Berke, Hicks and Tourney, 1993).

3.6.6 CATHODIC PROTECTION

The corrosion of reinforcement in concrete is an electrochemical process. Cathodic protection is a technique by which electrical potential of the steel is increased to a level at which corrosion cannot take place. It is widely used for both steel and concrete offshore structures, while on land it has been used for the protection of pipelines and similar structures. Two different methods are normally employed *viz.*, an impressed current sacrificial anodes.

In impressed current method, an impressed current is applied in opposite direction to nullify corrosion and convert the corroding metal from anode to cathode. Usually the impressed current is delivered from a direct current source like graphite, high silica iron, stainless steel or platinum. Usually a sufficient D.C. current is applied to an insoluble anode, buried in the soil impressed in the corroding medium and connected to the metallic structure to be protected. The anode is usually in backfill (composed of coke breeze or gypsum), so as to increase the electrical contact the surrounding soil. This type of cathodic protection has to be applied to water pins, condensers *etc.* this kind of protection techniques is particularly useful for large structure for long term operation.

In sacrificial anodes protection method, the metallic structures to be protected are connected by a wire to a more anodic metal so that the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly, while the parent structure, which becomes cathode, is protected. The corroded sacrificial anode block employed as sacrificial anodes are magnesium, zinc, aluminum and their alloys. Important applications of sacrificial anodic method include protection of buried pipeline, underground cables, marine structures, ship hulls, water tanks, piers etc. (Sheir, Jarman and Burstein, 2000).

3.6.7 ELECTROCHEMICAL REMOVAL OF CHLORIDE AND RE-ALKALIZATION

Chloride extraction and re-alkalization are nondestructive, electrochemical treatments to halt and prevent corrosion in chloride-contaminated and carbonated concrete, respectively. The process actually removes chloride ions from the contaminated concrete by the principle of ion migration while at the same time raising the pH of the carbonated concrete through electro-osmosis.

Concrete to be treated is first tested to determine the level of chloride contamination. Then, after preparing the surface, a steel or titanium mesh electrode is attached to the structure. The electrode is embedded in a nontoxic biodegradable electrolytic media. Next, electric contacts are established between the attached electrode and the steel reinforcement bars (rebars) inside the concrete. When an electric field is applied, chloride ions migrate away from the rebars and towards the externally attached electrode, eventually ending up in the temporary electrolytic media, which is then discarded. Simultaneously, alkali ions migrate from the electrolyte into the concrete, raising its pH to the original levels. The passivating layer of the rebars is thus re-established to protect them from corrosion.

This technique is akin to cathodic protection but unlike cathodic protection which requires a permanent installation, this techniques needs only a temporary installation lasting a few days. Using this technique 20% to 50% of the chloride present in concrete can removed. An electrical current in the range of 1 to 5 A/m^2 is needed. This treatment is most commonly applied to buildings with carbonation damage, but having at least moderate cover to the reinforcing steel ($\geq$10 *mm*) (Velivasakis, Henriksen and Whitmore, 1998; Garces, de Rojas and Climent, 2006).

3.6.8 USING BLENDED CEMENTS

Blended cement are produced by the addition of supplementary cementitious materials such as fly ash, slag, silica fume, rice husk ash, metakaolin *etc.* to ordinary Portland cement. This technology is well established globally to produce blended cements with ensured quality standards. Recently several important and major structures have been constructed with blended cements. These supplementary cementitious materials possess properties which impart certain desirable characteristics to the concrete mix which can enhance the strength and durability of concrete. Of course, a number of tests and a lot of processing of these materials need to be carried out before it can be suitably blended with cement (Hossain and Lachemi, 2003; Guneyisi, Qzturan and Gesoglu, 2006).

3.6.9 USING CHEMICAL CORROSION INHIBITORS

Numerous chemical admixtures, both organic and inorganic, have been suggested as specific inhibitors of steel corrosion in concrete. The initial work on corrosion inhibitors for concrete was done in the early 60's and some of the structures have been in place for over 20 *years* with no signs of deterioration. Unlike other protection methods that isolate the steel from the concrete, causing a loss of bond, corrosion inhibitors work with the natural corrosion protection mechanisms in concrete to protect the steel. The principle of most of the inhibitors is to develop a very thin chemical layer on steel surface that inhibit the corrosion attack.

As already mentioned in Section 2.4, there are generally three groups of inhibitors: anodic, cathodic and mixed inhibitors. Anodic inhibitors reduce the corrosion rate by reacting with the corrosion products and form a protective film. Cathodic inhibitors reduce the corrosion rate by reacting with the cathode sites (as an oxygen-barrier) on the steel. Mixed inhibitors both influence the anodic and cathodic reaction sites, by forming an adsorption film on the metal surface. Some of the admixtures, however, may retard or accelerate the setting time of the cement or be detrimental at later stage. Many would be subjected to leaching and hence less effective in concrete that has lost soluble material by leaching.

In recent years, many investigations have been undertaken on organic migrating corrosion inhibitor (MCI), which supposedly to forms a protective organic layer on the steel bars through chelation process (ACI-222; Nmai, Farrington and Bobrowski, 1992; Bobrowski, and Youn, 2000; Limaye, Angal and Radke, 2000; Broomfield, 2003). Some of the commercially available chemical inhibitors mentioned in literature have already been listed discussed in Section 2.4.

3.7 CONCLUDING REMARKS

Concrete normally provides excellent corrosion protection to the reinforcing steel. The high alkaline environment in concrete results in the formation of a tightly adhering film which passivates the steel and protects it from corrosion. In addition to this, concrete can be proportioned to have a low permeability which minimizes the penetration of corrosion inducing substances.

Despite these inherent properties, it is also a fact that many premature deterioration of concrete structure currently constitute a major concern for construction industry throughout the world. A number of failures of structures/structural element have been reported every year especially in last two to three decades. Parameters identified for such failures are poor quality of concrete, non-consideration of the service environment and change of exposure condition during the service life of the structure.

The reduction in the durability of composite can be attributed to the deterioration of matrix as well as of the reinforcement. Major factors behind the matrix weakening are carbonation, sulphate attack and reduction in alkalinity by leaching action. On the other hand non-homogeneity of the matrix, applied stress and depassivation of reinforcement by chloride ions are the main parameters governing the corrosion of steel in concrete. It is one of the major causes of deterioration in reinforced concrete structures. Corrosion is usually a slow process that develops at the reinforcing steel level, far from the naked eye assessment. Although slow, it is very dangerous and reduces the life time of the structure. may have severe safety implications and causes strong economic impact. Thus corrosion control plays an important role in the durability of reinforced concrete structures. The quality, safety and life time of reinforced concrete structures can be strongly improved if the correct measures concerning corrosion control are taken.

There are several methods reported in literature which help in evaluating the level of degradation of matrix. These methods include visual inspection, tests for the determination of the level of carbonation, alkali-silica reactivity and sulphate attack. Non-destructive testing also predicts the health of concrete. Some common tests in practice are resistivity measurement using four probe resistivity meter, ultrasonic pulse velocity technique radiography technique and infrared thermography technique. For the corrosion monitoring and estimation, prevalent methods are gravimetric weight loss method, open circuit potential (OCP) measurements, surface potential (SP) measurements, polarisation resistance method, impedance technique, harmonic analysis and noise analysis.

It has been concluded by various investigators that durable concrete can be produced if some points such as quality ingredients, adequate cover, careful design, good construction practices and reasonable limits on the amount of chloride in the concrete mix are ensured.

Other measures that have been suggested include the protective coating of reinforcement and to concrete surface; use of galvanized reinforcement and stainless steel bars; addition of chemical admixtures and blended cement in concrete; applying cathodic protection, electrochemical removal of chloride and re-alkalization. One of the most cost-effective solutions of reinforcement corrosion lies in the use of chemical corrosion inhibitors. Several inorganic and organic compounds have already been identified as potential corrosion inhibitors.

As the corrosion process is an electrochemical phenomenon, electrochemical techniques have been found to be useful for studying corrosion of rebars in concrete structures. The advantage of using electrochemical techniques lies in their simplicity and quickness. These can be easily implemented both in laboratory and field conditions. Among the various electrochemical techniques, the best one known for evaluation of instantaneous corrosion rate is the polarization resistance method and A.C. impedance spectroscopy. Gravimetric weight loss is regarded as one of the most effective and precise technique for quantifying the extent of corrosion. In this approach the assessment of corrosion is more accurate because the specimen is exposed to real conditions or simulated environment in the laboratory, over a much longer period of time.

In light of the above, it was decided to carryout screening of the corrosion inhibitors by polarization resistance method and A.C. impedance spectroscopy at the initial stage of the present study. Gravimetric weight loss method has been used for the evaluation of corrosion in ferrocement specimen exposed to longer duration.

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Chapter 4

Selection of Corrosion Inhibitors

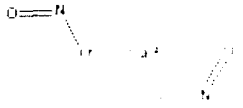
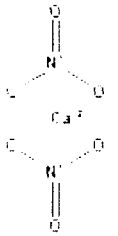
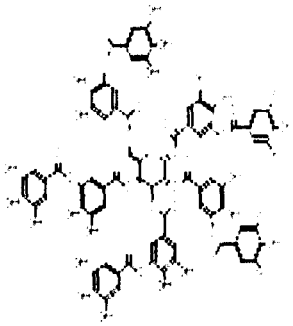
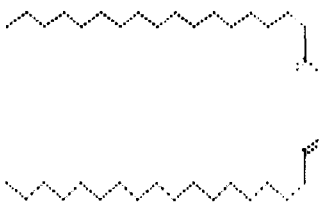
4.1 GENERAL

With the aim to prevent the corrosion in the ferrocement composites by using corrosion inhibitors and thereby improving the durability of the composites, a multi-stage scheme of investigation was undertaken as explained earlier in Chapter-1. The first stage of the study is aimed at investigating the effect of four corrosion inhibitors namely calcium nitrite, calcium nitrate, calcium stearate and tannic acid, on various parameters controlling the strength and durability of ferrocement. The effect of dose of corrosion inhibitors on setting time of cement; compressive and tensile strength of cement sand mortar was observed. Tests were also conducted on solutions to observe pH values at different concentrations of corrosion inhibitors. Electrochemical studies were carried out for the two concentrations of corrosion inhibitors *viz.* 1% and 5% by volume.

4.2 CORROSION INHIBITION MECHANISM OF SOME CORROSION INHIBITORS

Out of a number of available commercial corrosion inhibitors, two inorganic and two organic inhibitors were chosen for this study. Inorganic inhibitors were calcium nitrite and calcium nitrate, whereas organic inhibitors were tannic acid and calcium stearate. The details of these inhibitors in terms of chemical formula, molecular weight, molecular structure (Chem Finder, 2004; e Molecules, 2007) and manufacture brand are given in Table- 4.1.

Table- 4.1 Details of Corrosion Inhibitors Used for the Present Study

S. No.	Inhibitor	Chemical Formula	Molecular Weight	Brand	Molecular Structure
1.	Calcium Nitrite	$Ca(NO_2)_2$	132.0	Narang Chemicals	
2.	Calcium Nitrate	$Ca(NO_3)_2$	236.15	MERCK	
3.	Tannic Acid	$C_{76}H_{52}O_{46}$	1701.23	Glaxogen	
4.	Calcium Stearate	$C_{36}H_{70}CaO_4$	607.04	MERCK	

4.2.1 CALCIUM NITRITE

Calcium nitrite is the first corrosion inhibitor admixture commercialized on a large scale for reinforced concrete. It is identified as an anodic inhibitor because it functions at the anode, quickly oxidizing ferrous ions, the first product of corrosion, to ferric ions, which then precipitate in the alkaline pH of concrete.

The chemical reaction causing the corrosion inhibition is given as (Rosenberg and Gaidis, 1979):

$$Fe^{++} + 2OH^- + 2NO_2^- = 2NO\uparrow + Fe_2O_3 + H_2O \quad (4.1)$$

Calcium nitrite inhibits corrosion in concrete by reacting with the ferrous ions to form a film of Fe_2O_3 around the anode, precluding further corrosion. However, in the presence of chloride, nitrite and chloride engage in competing reactions, one inhibiting and the other accelerating the corrosion.

Gaidis (2004) suggested that in the presence of calcium nitrite, two more reactions are likely to occur in concrete as,

$$2NO + O_2 = 2NO_2 \quad (4.2)$$

$$2NO_2 + 2OH^- = NO_2^- + NO_3^- + H_2O \quad (4.3)$$

Of the equal interest are the reactions which do not proceed to any extent,

$$Fe^0 + NO_2^- = Fe^0 + NO_2^- \quad (4.4)$$

$$Fe^{+++} + NO_2^- = Fe^{+++} + NO_2^- \quad (4.5)$$

The stability of ferric ions in the presence of nitrite was proven by mixing solutions of ferric sulphate and calcium nitrite and filtering off the calcium sulphate precipitate. The resultant solution of ferric nitrite, kept in a clear glass bottle exposed to laboratory fluorescent light for over 15 *years*, only slowly developed a minimal black precipitate (Gaidis, 2004).

4.2.2 CALCIUM NITRATE

The corrosion inhibition mechanism of calcium nitrate is considered similar to that of corrosion inhibition by nitrite. Justnes and Nygaard (1994) observed that calcium nitrate is an effective corrosion inhibitor and propounded that the nitrate (NO_3^-) inhibits corrosion by transforming ferrous hydroxide ($Fe(OH)_2$) to ferric hydroxide ($Fe(OH)_3$), which is assumed to be more protective. They prefer the use of calcium nitrate, as larger quantities of ferrous hydroxide are oxidized to ferric hydroxide. Further, it is more readily available and less expensive. The following chemical reactions describe the corrosion inhibition mechanism:

$$2NO_3^- + 2H_2O + 4e^- = 2NO_2^- + 4OH^- \qquad E_0 = +0.01\,V \qquad (4.6)$$

$$2Fe(OH)_2 + NO_3^- + H_2O = 2Fe(OH)_3 + NO_2^- \qquad E_0 = +0.57\,V \qquad (4.7)$$

Gaidis (2004) reviewed the reported literature on corrosion inhibition mechanism of calcium nitrate and concluded that nitrates do not have the extensive history of corrosion inhibition in concrete that nitrites have. It may be because of the fact that in spite of a superficial chemical resemblance to calcium nitrite, corrosion inhibition by calcium nitrate could occur by an entirely different process, perhaps one dependent more on the improved properties of the concrete. Further, unlike nitrite, nitrate does not appear to work when tested in a rapid solution test.

A good reason for continuing the investigation of calcium nitrate as a corrosion inhibitor is its easy availability and lower cost. Its widespread use as an accelerator suggests that at least it is not harmful to concrete (except in very concentrated form). The acceleration in set may be accompanied by a temporary compressive strength loss at 1 *day*, but the strength loss is quickly regained. While the electrochemical data and visual examination are all encouraging, more work is needed to determine the mechanism behind the improvement in corrosion resistance.

4.2.3 TANNIC ACID

Tannin, usually in the form of a yellowish-white or pale brown powder, is obtained from fermented oak galls by extraction with water-saturated ether. Tannic acid, a commercial form of tannin, is a polyphenol. Tannic acid is soluble in water, alcohol, and acetone, and gives precipitates with most metallic salts, proteins, and alkaloids. Chemically, it is a penta-m-digalloyl-glucose having a high molecular weight (Merck Index, 1976; Dictionary of Descriptive Terminology, 2007; Wikimedia Foundation, 2007).

Apart from various other uses, tannic acid is also recognized as a potential organic corrosion inhibitor. The effectiveness of the organic inhibitor depends mainly on bonding strength to metal surface; aromaticity; and/or conjugated bonding, nature and number of bonding atoms. These inhibitors act by adsorbing onto the metal surface, thus providing a barrier to the corrosive environment. The other advantages of organic corrosion inhibitors are:

- Inhibitors adsorb and form a thin polymeric layer.
- Presence of film prevents uniform corrosion attack.
- Organic inhibitors increase the activation energy on the metal surface.
- Organic inhibitors eliminate corrosion over wide range of pH values.

There are a large number of research contributions on the properties and effect of coatings of tannic acid on steel as a corrosion inhibitor. In neutral solutions, tannic acid was found to form a protective layer as a result from the reaction between tannic acid and iron ions. However, there is controversy over the possible solubility of these coatings and also the extent of their inhibitive properties. When tannic acid is used with steel, iron tannates and tannate complexes are formed with the metal or its oxides, in a self-catalysed reaction. The corrosion inhibition is mainly attributed to improved adherence of these complexes on metal surfaces. A few investigators reported that even though some initial improvement in protection is found, the inhibition is small, concluding that the coating eventually dissolves in aqueous solution. (Morcillo, *et al.* 1992; Feliu *et al.*, 1993; Matamala, Smeltzer and Droguett, 1994; Al-Mayouf, 1997; Smit, 2003).

Flis and Zakroczymski (1996) studied the inhibition performance of tannin in simulated concrete pore solution along with chloride ions by electrochemical methods and concluded that the tannin slows down the changes in R_{ct} and C_{dl} and found that the protection is due to the film formation of tannin-Fe (III) chelate at the outer surface.

Sarc and Kapor (1999) established the effectiveness of tannic acid in slowing down the corrosion process. The cathodic inhibition was recognised by the slowing down of the cathodic current of the polarisation run. Soluble iron tannate chelate has been observed as a dark blue flux flowing down from the metal surface into solution of tannin in the tap water, resulting in a corrosion process. Tannin decreases the pH of tap water. Calcium gluconate added in tannin solutions increases the pH maintaining it in the near neutral region and thus enabling the precipitation of a low soluble protective iron tannate and metal gluconate.

4.2.4 CALCIUM STEARATE

Calcium stearate is a compound of calcium with a mixture of solid organic acids or some fatty acids obtained from edible sources. It is generally used as a solid-phase lubricant that reduces friction between particles of the substance to which it is added. Calcium stearate is also known as a cathodic/mixed type corrosion inhibitor for reinforced concrete (U.S. Patent, 1996), but not very popular. Cathodic inhibitors act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas of the surface. Mixed inhibitors work by reducing both the cathodic and anodic reactions. They are typically film forming compounds that cause the formation of precipitates on the surface. Apart from being used as corrosion inhibitor and water repellent admixture in cement, it is being applied in wide range of fields such as flatting agent in paints, stabilizer for polyvinyl resins, food additive, mold release agent, and in emulsions and cosmetics (Eco Chemie, 2007).

4.3 EFECT OF CORROSION INHIBITORS ON PHYSICAL PROPERTIES OF CEMENT

Tests were conducted to determine setting time, compressive strength and tensile strength of cement in accordance with the relevant Indian standard code of practices with the objective to ascertain the effect of the various concentrations of the corrosion inhibitors in matrix on these physical properties.

4.3.1 CONSTITUENT MATERIALS FOR TESTS ON PHYSICAL PROPERTIES OF CEMENT

The properties of the constituents materials *viz.* cement, sand and water, for determining the setting time, compressive and tensile strength of cement are given below.

4.3.1.1 CEMENT

Ordinary Portland cement of 43 Grade was used throughout the investigation. The physical properties of the cement were determined in the laboratory as per IS: 8112-1989 and IS: 4031(Part 5 & 6)-1988. For the determination of compressive and tensile strength of cement sand mortar, standard sand was used as per the provisions of relevant code. The physical properties of the cement are given in the Table- 4.2.

4.3.1.2 SAND

Locally available coarse sand was used for casting all other test specimens. The grading and fineness modulus of the sand are given in Table- 4.3. Lumps of clay and other foreign matter were separated out from the sand and it was later washed with water and then air dried. The fineness modulus was determined using the sieve analysis as 2.30. The density of loose sand was 12.73 kN/m^3 and that for compacted sand was 13.92 kN/m^3.

4.3.1.3 WATER

Potable water was used for mixing and curing of specimens. The properties of the potable water used for the present study are given in Table- 4.4.

Table- 4.2 Physical Properties of Cement

S. No.	Properties		Values	Recommended Value
1.	Fineness determined by sieving the cement through Indian Standard 90 *micron* sieve		9.5%	10.0%
2.	Normal Consistency		30%	--
3.	Setting time (*minutes*)	Initial	143	>30
		Final	343	<600
4.	Compressive strength (N/mm^2)	At 3 *days*	23.1	23
		At 7 *days*	33.2	33
		At 28 *days*	43.3	43
5.	Tensile strength (N/mm^2)	At 3 *days*	2.28	2.0
		At 7 *days*	2.62	2.5
		At 28 *days*	2.85	---

Table- 4.3 Sieve Analysis of Fine Aggregate (Sand)

S. No.	Sieve Size	% Weight Retained	% Cumulative Weight Retained	Recommended Value for % Cumulative Weight Retained *
1.	4.75 *mm*	Nil	0.0	0.0
2.	2.36 *mm*	0.3	0.3	0–20
3.	1.18 *mm*	23.2	23.5	15–50
4.	600 *micron*	20.9	44.4	40–75
5.	300 *micron*	36.7	81.1	60–90
6.	150 *micron*	16.6	97.7	90–98

* Ferrocement Model Code (2001)

Table- 4.4 Properties of Potable Water Used

S. No.	Properties	Value	Desirable Limit
1.	pH	7.53	6.5–8.5
2.	Turbidity	0.173	5
3.	Total Dissolved Solids (TDS) (*mg/l*)	264	500
4.	Total hardness (*mg/l*)	250	300
5.	Calcium hardness (*mg/l*)	64	75
6.	Magnesium hardness (*mg/l*)	21.6	30
7.	Iron (*mg/l*)	0.0712	0.3
8.	Chloride (*mg/l*)	17.49	250
9.	Sulphate (*mg/l*)	31.3	200
10.	Nitrate (*mg/l*)	9.68	45
11.	Flouride (*mg/l*)	0.227	1
12.	Sodium (*mg/l*)	24.7	--
13.	Phosphate (*mg/l*)	0.03	--
14.	Cadmium (*mg/l*)	0.001	0.01
15.	Chromium (*mg/l*)	0.0086	0.05

4.3.2 EFFECT ON SETTING TIME

Setting time was determined using a dash pot fitted Vicat's apparatus (Gauge Instruments, Delhi, India). For all the four corrosion inhibitors *viz.* calcium nitrite, calcium nitrate, tannic acid and calcium stearate, setting time was observed keeping the dose of inhibitors as 1%, 3% and 5% by weight of cement in each case. The test were conducted in accordance with IS: 4031(Part 5) and the results are given in Table- 4.5.

4.3.3 EFFECT ON COMPRESSIVE STRENGTH

The tests for compressive strength were conducted in accordance with IS: 4031(Part 6). Mortar cubes of size 70.6×70.6×70.6 *mm* were cast (Fig. 4.1). The dose of the inhibitors was kept as 1%, 3% and 5% by weight of cement in each case. The mortar cubes were cast in triplicate and cured till the time of test. Two groups of control specimens were used for the comparison of results. For the first group, the specimens were cured in potable water and for the second group, the control specimens were cured in saline water (4% *NaCl* solution). All inhibited specimens were cured in potable water only. The compressive strength was observed at 3, 7, 14, 28 and 90 *days*. A cube under test is shown in Fig. 4.2. The specimens were tested in the compressive strength testing machine (AIMIL Ltd., New Delhi, India, having 1000 *kN* capacity with a least count of 1 *kN*). The values of the compressive strength are given in Table- 4.6. A comparison of the compressive strength values of the mortar cubes prepared by adding varying doses of corrosion inhibitors has been made in Figs. 4.3 – 4.6.

Table- 4.5 Effect of Corrosion Inhibitor on Setting Time of Cement

S. No.	System	Initial Setting Time (*minutes*)	% Variation	Final Setting Time (*minutes*)	% Variation
1.	Blank (Potable water)	143	--	343	--
2.	1% Calcium Nitrite	104	-27.0	309	-09.9
3.	3% Calcium Nitrite	146	+02.1	320	-06.7
4.	5% Calcium Nitrite	238	+66.4	384	+11.9
5.	1% Calcium Nitrate	75	-47.5	155	-54.8
6.	3% Calcium Nitrate	68	-52.4	125	-63.5
7.	5% Calcium Nitrate	45	-68.5	110	-67.9
8.	1% Tannic Acid	32	-77.6	300	-12.5
9.	3% Tannic Acid	33	-76.9	360	+04.9
10.	5% Tannic Acid	39	-72.7	550	+60.35
11.	1% Calcium Stearate	39	-72.7	152	-55.68
12.	3% Calcium Stearate	45	-68.5	180	-47.52
13.	5% Calcium Stearate	56	-60.8	230	-32.9

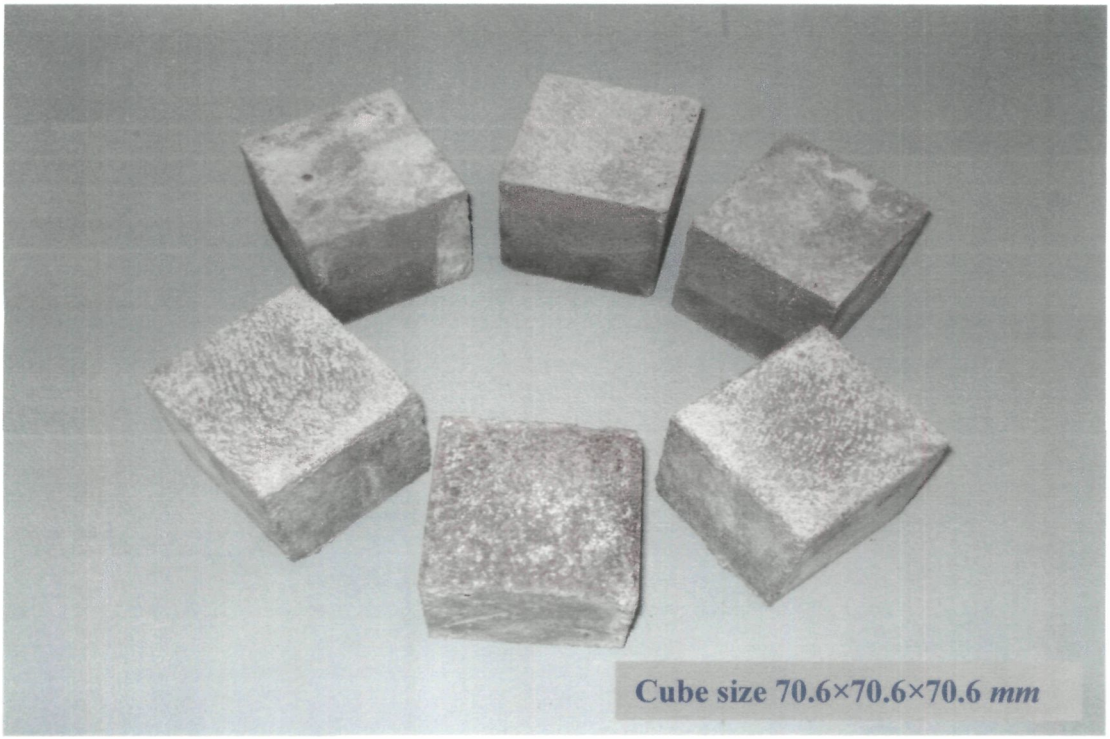


Fig. 4.1 Mortar Cubes for Compressive Strength Test

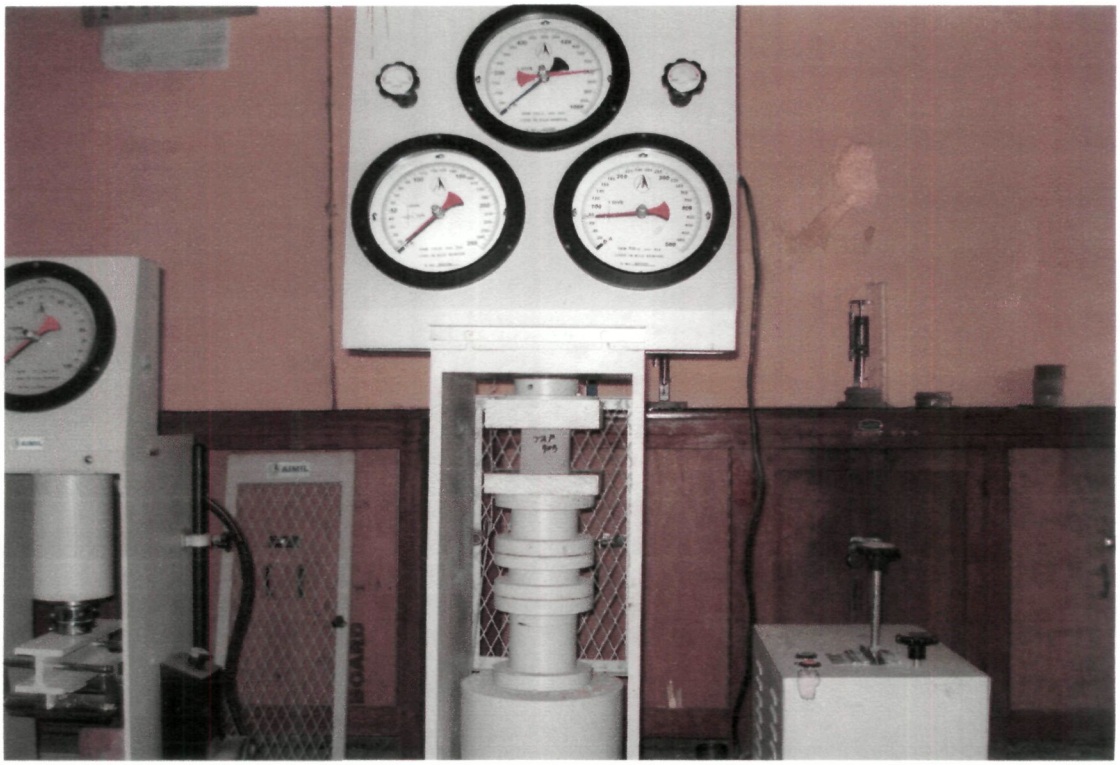


Fig. 4.2 Mortar Cubes under Compressive Strength Test

Table- 4.6 Effect of Corrosion Inhibitor on Compressive Strength of Mortar

S. No.	Specimen Description	Compressive Strength of Mortar Cube N/mm^2				
		3 *days*	7 *days*	14 *days*	28 *days*	90 *days*
1.	Control (Potable water)	16.1	26.0	37.2	43.4	48.1
2.	Control (Saline water)	15.0	24.7	33.3	38.2	41.6
3.	1% Calcium Nitrite	15.9	18.2	26.0	42.6	43.4
4.	3% Calcium Nitrite	16.1	19.5	30.2	46.5	48.0
5.	5% Calcium Nitrite	16.4	25.5	30.9	46.8	48.2
6.	1% Calcium Nitrate	14.8	21.6	24.2	36.1	51.8
7.	3% Calcium Nitrate	15.6	28.6	35.9	44.2	52.0
8.	5% Calcium Nitrate	18.5	28.6	40.8	46.3	52.4
9.	1% Tannic Acid	10.4	20.8	26.5	39.9	48.0
10.	3% Tannic Acid	2.6	10.4	15.6	21.8	31.2
11.	5% Tannic Acid	2.6	7.8	13.0	18.2	24.1
12.	1% Calcium Stearate	14.3	20.8	28.6	34.1	41.6
13.	3% Calcium Stearate	10.4	20.5	28.6	31.2	42.4
14.	5% Calcium Stearate	8.6	19.8	27.6	29.9	40.6

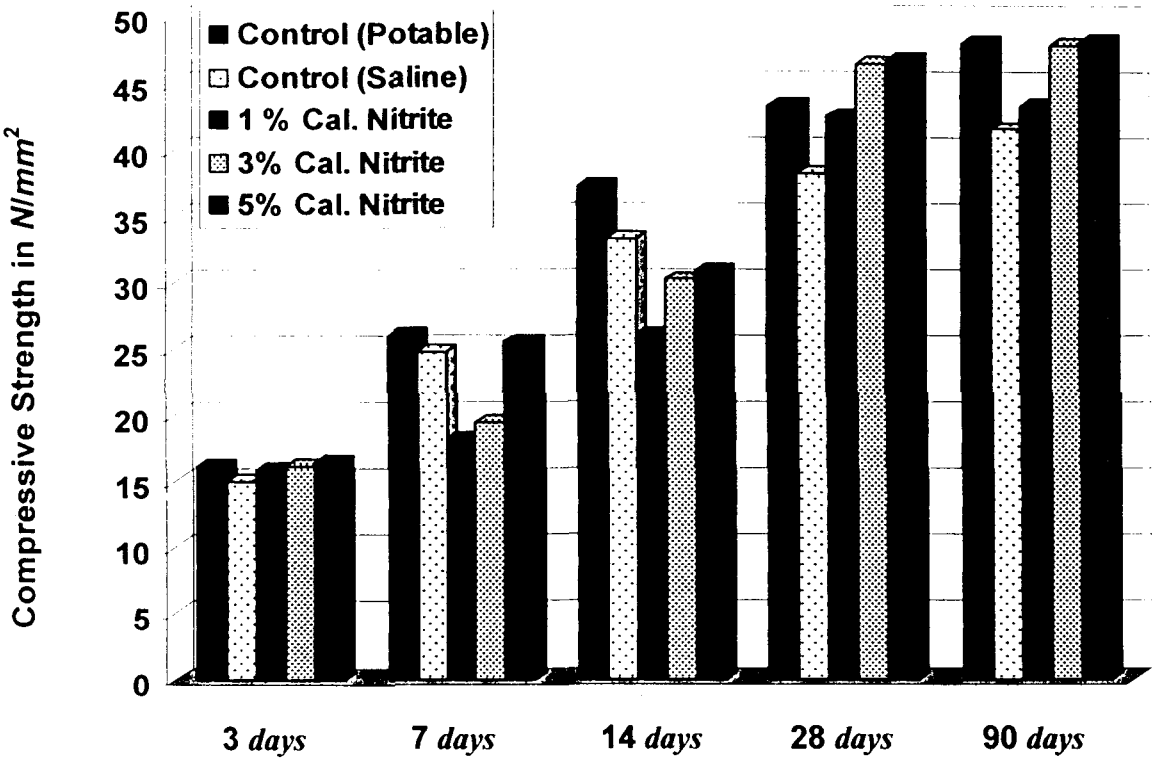


Fig. 4.3 Compressive Strength of Mortar Cube with 1%, 3% and 5% Calcium Nitrite

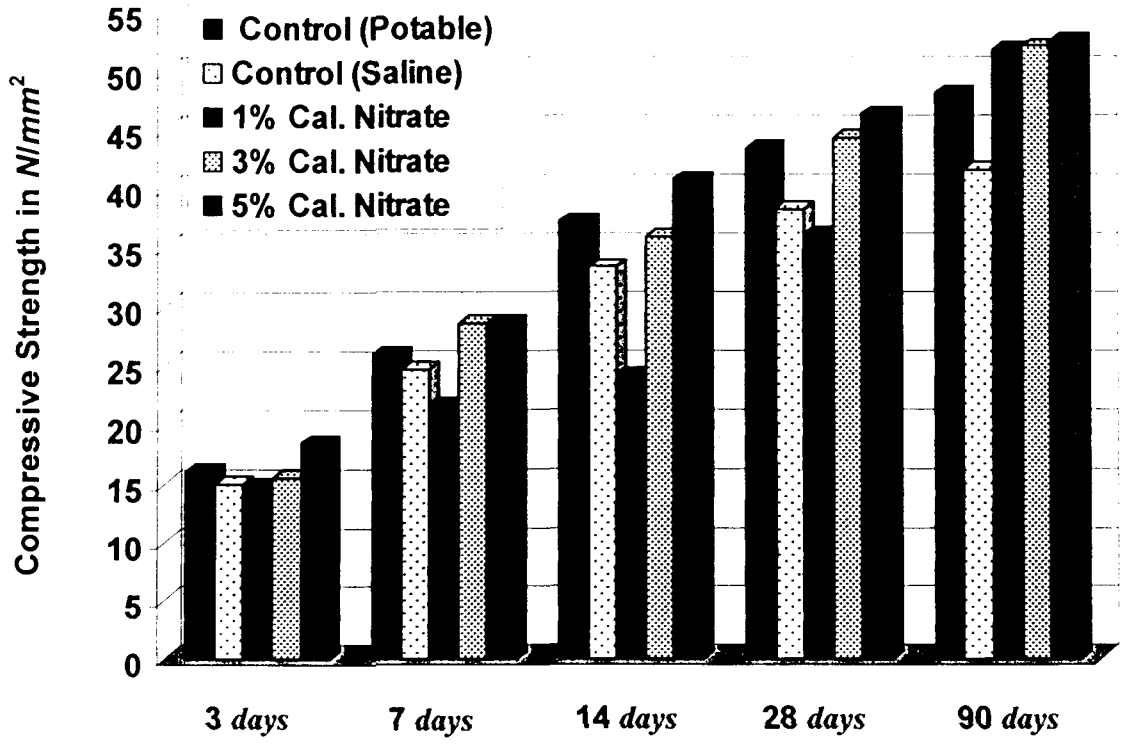


Fig. 4.4 Compressive Strength of Mortar Cube with 1%, 3% and 5% Calcium Nitrate

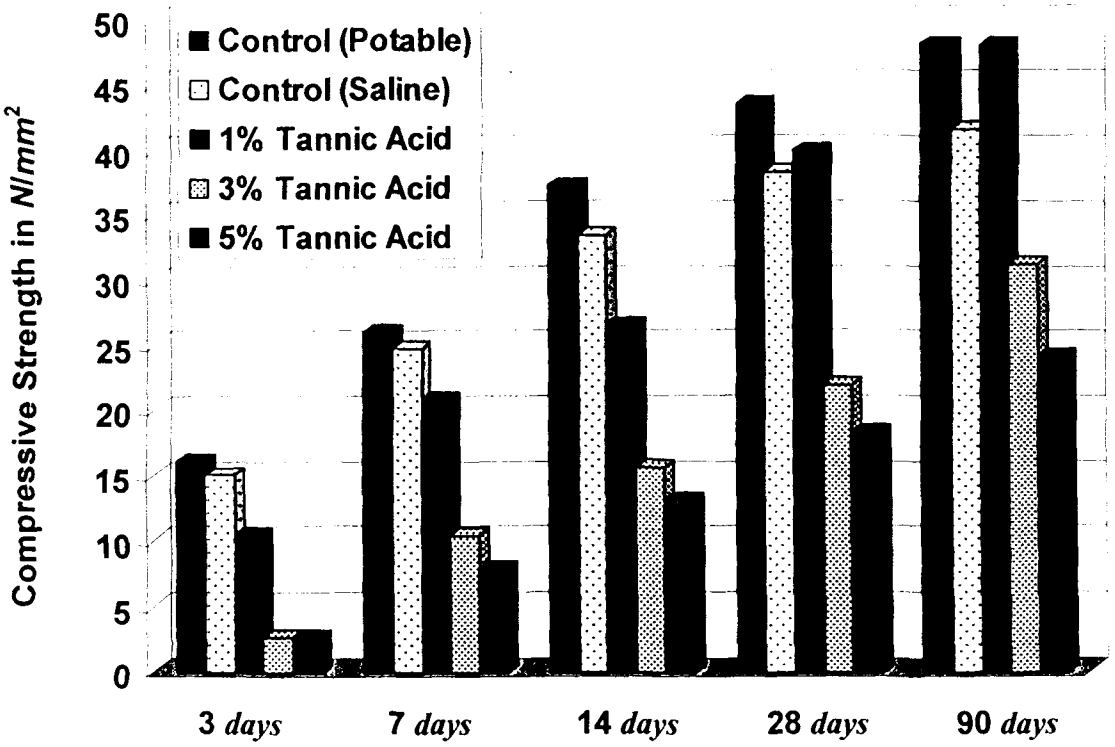


Fig. 4.5 Compressive Strength of Mortar Cube with 1%, 3% and 5% Tannic Acid

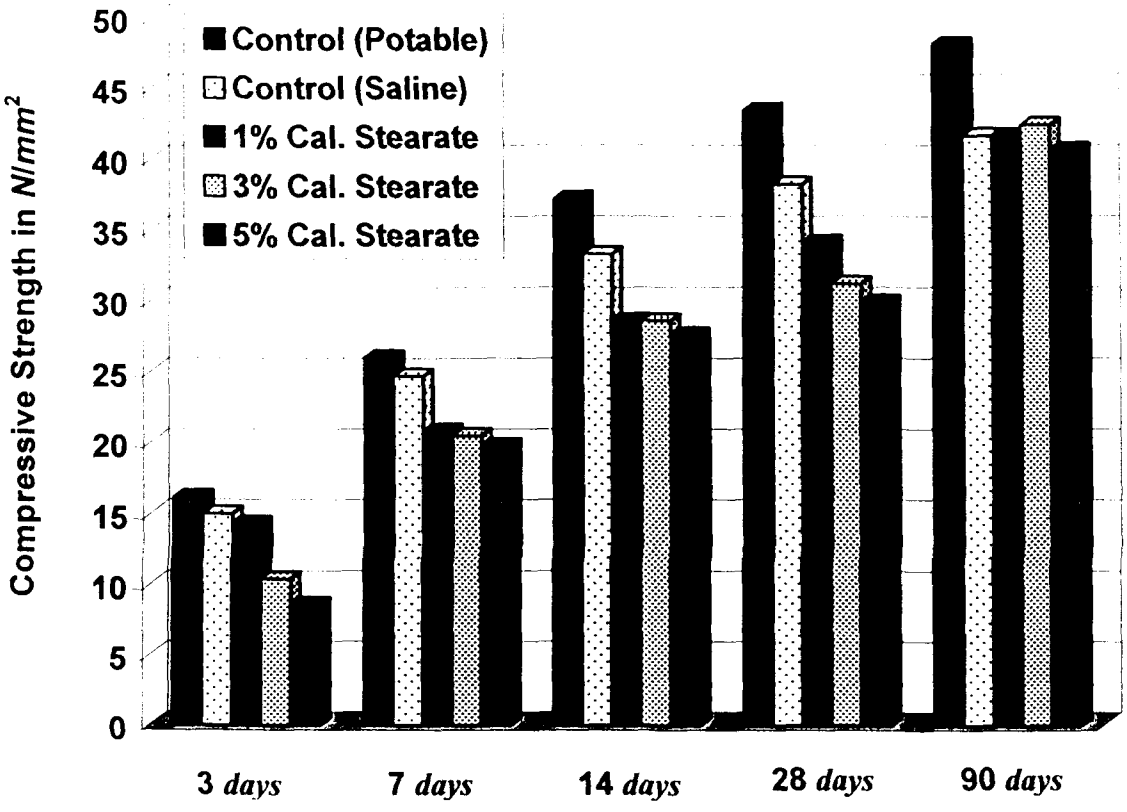


Fig. 4.6 Compressive Strength of Mortar Cube with 1%, 3% and 5% Calcium Stearate

4.3.4. EFFECT ON TENSILE STRENGTH

For determining the tensile strength, mortar briquette with details shown in Fig. 4.7, were cast in triplicate in varying doses of corrosion inhibitors. The doses of corrosion inhibitors, curing condition and curing time were kept same as explained in the Section 4.3.3. The cast briquettes are shown in Fig. 4.8. The briquettes were cured till the time of test. The tensile strength was observed at 3, 7, 14, 28 and 90 *days* using a briquette tensile strength testing machine of Avery Ltd., U.K.. The current IS code is silent with regard to the tensile strength test on cement sand mortar. However, in the past it used to be a popular test (IS: 269, ASTM: C-190). The literature dealing with the ferrocement characteristics recommends dumble-shaped test specimen for the determination of tensile strength (Shah and Balaguru, 1984). Since the mortar under investigation has to be used for the preparation of ferrocement test specimen, it was thought that this test would at least give an idea about the effect of addition of the corrosion inhibitors on the tensile characteristics of the cement mortar and therefore the tests was undertaken. The values of the tensile strength are given in Table- 4.7. A comparison of the tensile strength values has been made in Figs. 4.9 – 4.12.

Table- 4.7 Effect of Corrosion Inhibitor on Tensile Strength of Mortar

S. No.	Specimen Description	Tensile Strength of Mortar Briquette in N/mm^2				
		3 *days*	7 *days*	14 *days*	28 *days*	90 *days*
1.	Control (Potable Water)	2.28	2.62	2.62	2.85	2.91
2.	Control (Saline Water)	2.30	2.30	3.20	3.20	4.12
3.	1% Calcium Nitrite	2.26	2.53	2.69	2.96	3.42
4.	3% Calcium Nitrite	2.30	2.64	2.80	3.25	3.52
5.	5% Calcium Nitrite	2.72	2.70	3.20	3.63	3.68
6.	1% Calcium Nitrate	1.65	2.05	2.51	3.12	4.32
7.	3% Calcium Nitrate	2.29	2.74	2.96	3.65	4.50
8.	5% Calcium Nitrate	3.31	3.42	3.65	4.22	5.07
9.	1% Tannic Acid	1.14	1.60	2.00	2.40	3.48
10.	3% Tannic Acid	0.23	0.80	1.38	1.76	1.90
11.	5% Tannic Acid	0.11	0.34	0.80	1.14	1.25
12.	1% Calcium Stearate	1.54	2.40	2.56	2.80	4.21
13.	3% Calcium Stearate	1.50	2.22	2.45	2.74	3.62
14.	5% Calcium Stearate	1.49	2.14	2.40	2.62	3.31

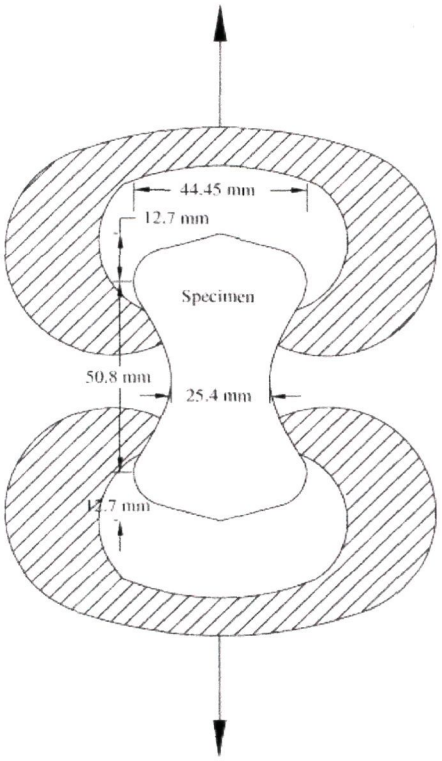


Fig. 4.7 Dimensional Details of Mortar Briquettes for Tensile Strength Test (IS: 269, ASTM C-190)

Fig. 4.8 Mortar Briquettes for Tensile Strength Test

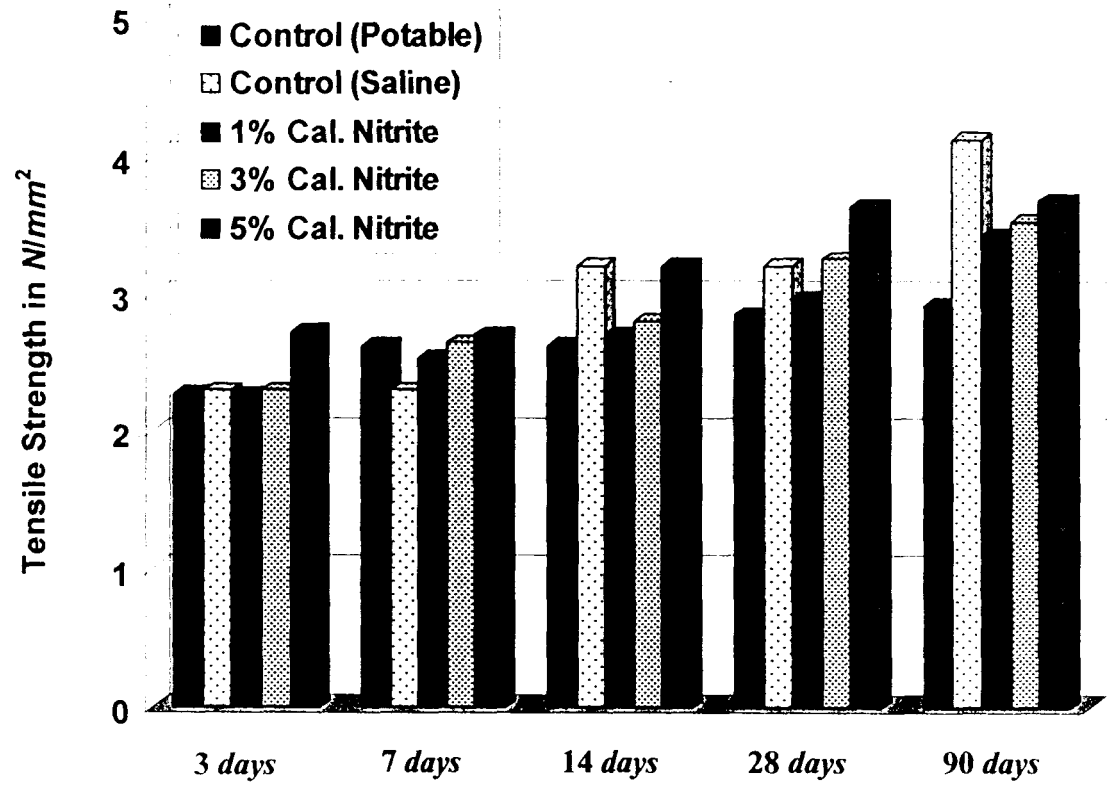


Fig. 4.9 Tensile Strength of Mortar Briquettes with 1%, 3% and 5% Calcium Nitrite

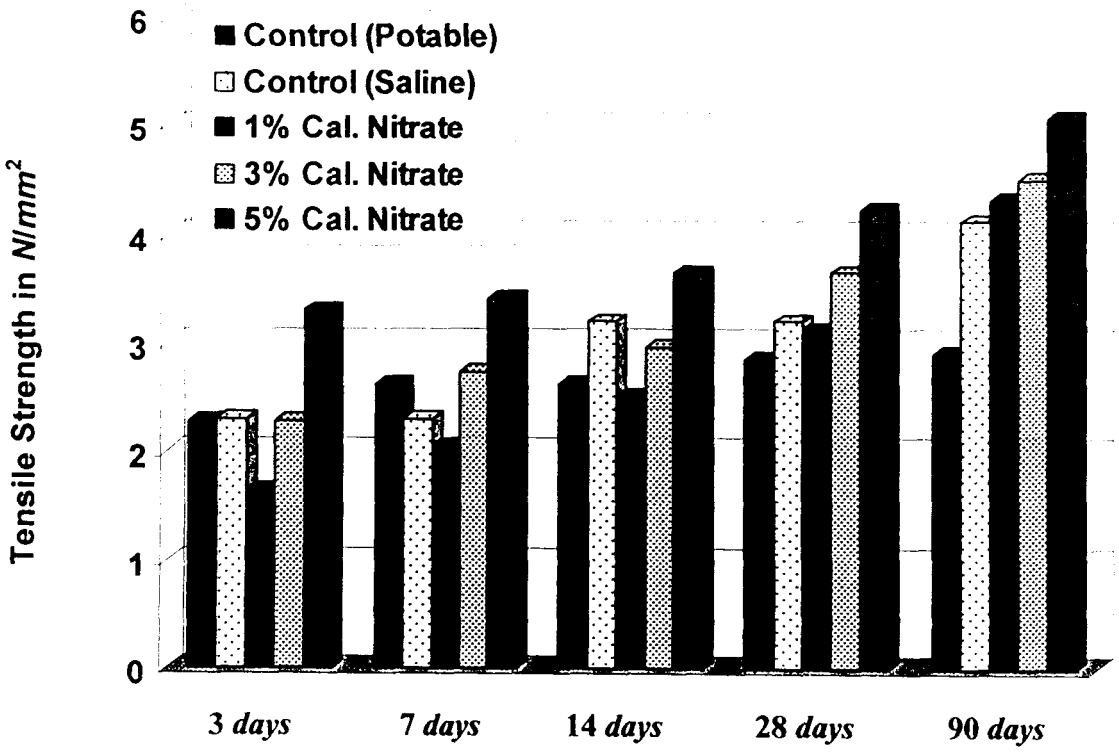


Fig. 4.10 Tensile Strength of Mortar Briquettes with 1%, 3% and 5% Calcium Nitrate

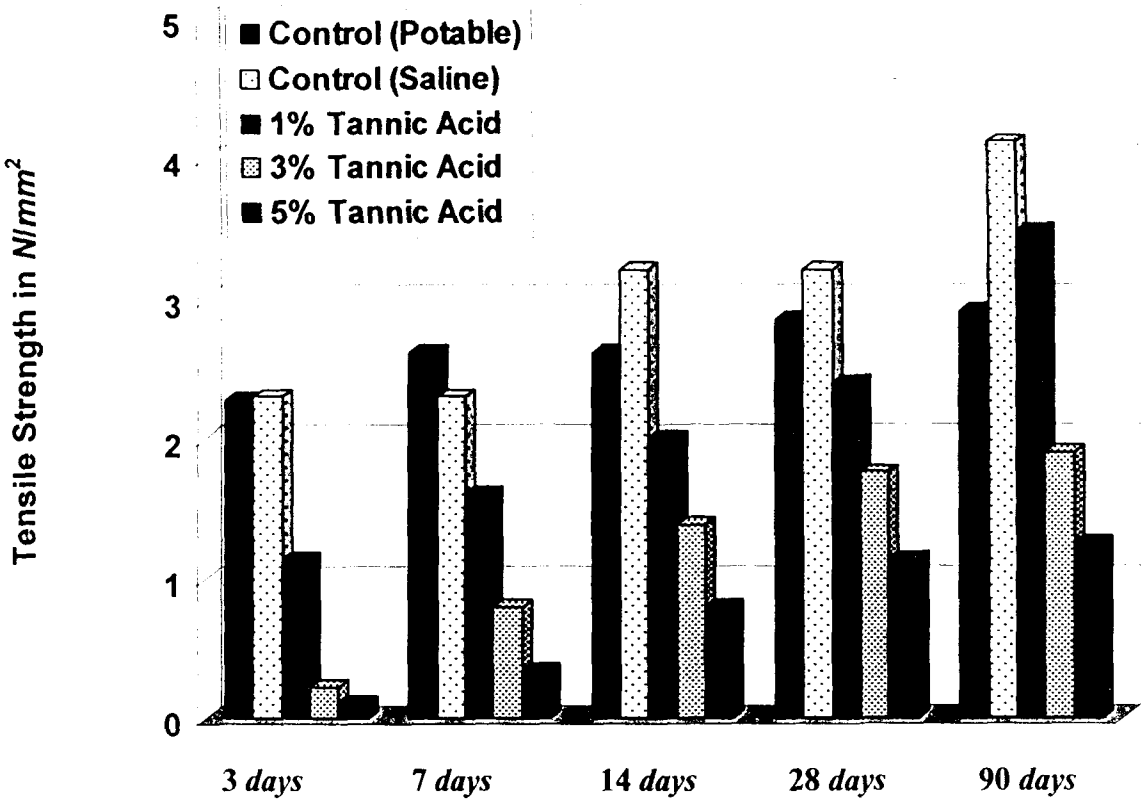


Fig. 4.11 Tensile Strength of Mortar Briquettes with 1%, 3% and 5% Tannic Acid

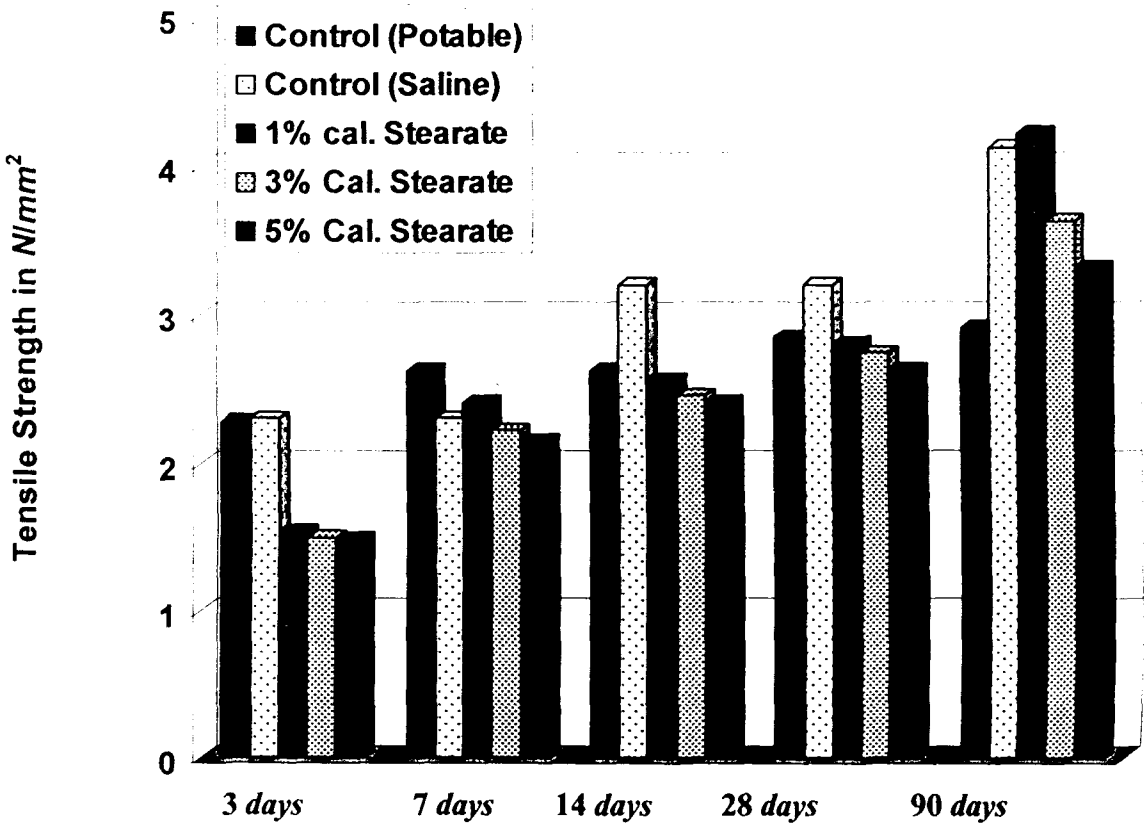


Fig. 4.12 Tensile Strength of Mortar Briquettes with 1%, 3% and 5% Calcium Stearate

4.3.5 DISCUSSION ON TEST RESULTS

Setting time test on cement paste; and compressive strength and tensile strength test on cement sand mortar were conducted to observe the effect of the addition of the four corrosion inhibitors on their properties. The tests results presented in previous sections are discussed below:

4.3.5.1 SETTING TIME

It has been observed that all the four inhibitors act as an accelerator for the initial setting except for the 3% and 5% dose of calcium nitrite which retard the setting time by 2.1% and 66.2% respectively as compared to the control values.

A reduction of 27% in initial setting time has been observed when 1% calcium nitrite was added. However a very nominal increase of 2% was found in initial setting time at the addition of 3% calcium nitrite. In final setting time, a marginal reduction of 9.9% and 6.7% respectively, were observed at the addition of 1% and 3% calcium nitrite. respectively. An increase of 11.9% has been observed for 5% calcium nitrite dose.

Maximum acceleration of both the initial and final setting has been found with the addition of calcium nitrate and calcium stearate. The rate of acceleration has been increases with the increase in the dose of the calcium nitrate. However, an opposite trend was observed for the calcium stearate. A reduction of 47%, 5%, 52.4% and 68.5% respectively, in initial setting time and 54.8%, 63.5% and 67.9% respectively, in final setting time was found when 1%, 3% and 5% of the calcium nitrate was added. The reduction observed for calcium stearate has been 72.7%, 68.5% and 60.8% respectively in the initial setting time and 55.7%, 47.5% and 32.9% respectively in the final setting time for the respective dose of 1%, 3% and 5%.

Tannic acid has also been found to accelerate the initial setting. The reduction in initial setting time is 77.6%, 76.9% and 72.7% respectively when 1%, 3% and 5% of the inhibitor is added. Except at 1% dose, for which the final setting time has been reduced by 12.5%, an increase of 4.9% and 60.3% in the value has been observed for the addition of 3% and 5% of the tannic acid.

It is important to mention here that whether the inhibitor acted as accelerator or retarder, the values of the initial and final setting time are within the recommended limits of the code of practice.

In the first part of the study initial setting time has been determined with the varying dose of corrosion inhibitors as explained in Section 4.3.2. It has been observed that most of the inhibitors acted as accelerator to the initial and final setting though the rate of acceleration was different in each case. It is believed that the accelerating admixture basically accelerates and retarding one retards the rate of reaction of tri-calcium aluminate (C_3A) with water *i.e.* hydration process. However, it was interesting to note that at higher doses some of the inhibitor (5% calcium nitrite and tannic acid) behaved as retarders. This observation is in line with the findings reported by Mehta (1986). It is perhaps due to the fact that the accelerating admixture promotes the dissolution of the cations (calcium ions) and anions from the cement. Since there are several anions to dissolve, the accelerator should promote the dissolving of that constituent which has the lowest dissolving rate during the early hydration period (*e.g.* silicate ions). A retarding admixture impedes the dissolution of the cement cations and anions, preferably those anions which have the highest dissolving rate during the early hydration period (*e.g.* aluminate ions).

The presence of strong cations in the solution (*i.e.* K^+ or Na^+), reduces the solubility of silicate and aluminates ions. In small concentration, the former effect is dominant and in large concentrations the later effect becomes dominant. Similarly in presence of strong anions in solution (*i.e.* Cl^-, NO_3^-, SO_4^{--}) reduces the solubility of less strong anions (*i.e.* silicates and aluminates) but tends to accelerate the solubility of calcium ions. In small concentrations, the former effect is dominant, in large concentrations, the later effect becomes dominant. This mechanism is perhaps instigating the acceleration at lower dose and retardation at higher dose.

4.3.5.2 COMPRESSIVE STRENGTH

Since the matrix used in ferrocement is cement sand mortar, hence, the strength of this matrix is expected to play a major role in strength of ferrocement structural elements. With this in view, compressive strength test were conducted on cement sand mortar cubes to observe the effect of the addition of the four corrosion inhibitors in the matrix.

A general trend of increase in compressive strength with time has been observed for all the category of specimens. A marginally lower value of compressive strength has been noticed for cubes cured in saline water as compared to the control specimen cured in potable water.

It has been observed that with the increase in the dose of calcium nitrate from 1% to 3%, compressive strength of the cubes increases appreciably, however, with further increase in the dose of calcium nitrite to 5%, a relatively marginal increase has been observed. This trend has been found to be consistent at all the ages of observations. The strength of the cubes with 1%, 3% and 5% of calcium nitrite has been found to be comparable with the control specimen. Except for 7 and 14 *days* compressive strength for a few of the doses of calcium nitrite, where lower value has been observed, the strength at all other ages are quite comparable with the control specimen. A steady increase in compressive strength with age has been observed for all the doses of calcium nitrite.

Compressive strength has been found to increase as the dose of the calcium nitrate has been increased from 1% to 3%; however the strength increases marginally or remains same with further increase of calcium nitrate dose to 5%. At 1% dose of calcium nitrate inhibitor, a reduction in compressive strength up to 28 *days* has been observed, however surprisingly very high value, even higher than the control specimen, has been observed at 90 *days*. The value of compressive strength remains comparable with the control specimen at all ages for the 3% and 5% dose of the calcium nitrate.

A reduction in the value of compressive strength has been observed with the increase of the dose of calcium stearate. Though with age, an increase in strength has been found but the values remain lower than the corresponding values of control specimen.

4.3.5.3 TENSILE STRENGTH

It has been observed that with the increase in the dose of calcium nitrate, tensile strength of the cement sand mortar briquettes increases appreciably. This observation has been found to be consistent at all the ages of observations. The strength of briquettes with 1% calcium nitrite has been found to be comparable up to 14 *days*, thereafter a significant increase has been observed. However for briquettes with 3% and 5% of calcium nitrite, at all the ages of test, values higher than the control briquettes have been found. A steady increase in tensile strength with age has been observed for all the doses of calcium nitrite.

Almost similar trend as that of calcium nitrite has been found in case of calcium nitrate for 1% and 3% inhibitor dose. However for 5% calcium nitrate dose an increase of about 40-70% has been observed in the tensile strength.

At 1% dose of tannic acid, the tensile strength at 3, 7, 14 and 28 *days* is found to be lower than the control specimen values at these ages, whereas the same at 90 *days* is observed to be higher than the tensile strength of the control briquette at 90 *days*. The tensile strength for specimens with 3% and 5% dose of tannic acid, is observed to be much lower than the control specimens of the same age. Even after 90 *days* the tensile strength remains far below the level of the control specimen. The mix using 1% tannic acid exhibits a delayed increase in the tensile strength, which up to 28 *days* partially lags behind the control specimen values and becomes equal to control specimen tensile strength value at 90 *days*.

A very negligible variation in the value of tensile strength has been observed with the increase of the dose of calcium stearate. Though with age, an increase in strength has been found but the values remain lower than the corresponding values of control specimen up to an age of 28 *days*. However, when compared at 90 *days* the tensile strength has been found to be higher than the control specimen.

Broadly speaking a very normal increase in compressive and tensile strength with age has been observed for the control, saline and most of the mortar mixes having different percentages of the corrosion inhibitors. However, in some of the cases it has been observed that the early gain in strength is much lower than the control specimen. This observation is especially valid for the specimens containing 3% and 5% dose of tannic acid and calcium stearate. It is known that a freshly set Portland cement paste has little or no strength because it represents only the beginning of the hydration of tri-calcium silicate (C_3S) reaction which continues rapidly for several weeks. The process of progressive filling of the void spaces in the paste with the reaction products results in a decrease in porosity and permeability, and an increase in strength. Early strength at 3, 7 and 28 *days* strength is mainly contributed by C_3S, however major contributor of the strength beyond 28 *days* is di-calcium silicate (C_2S). Slow gain in strength at early age in some of the combinations can be attributed to the slow down of the reaction of C_3S by the addition of these chemicals in high concentration.

Similarly the significant increase in strength after 28 *days*, in few of the combinations has been observed, specially for calcium nitrate. It is perhaps due to the fact that the C_3S reaction gains momentum only beyond 28 *days*. These chemicals might be acting as a catalyst to the C_2S reaction too, which also contributes to the gain in delayed strength.

4.4 EFFECT OF CORROSION INHIBITORS ON pH OF EXPOSURE MEDIUMS

The level of pH in cementitious composite is normally around 12–13. The protective system created by the formation of a passive iron oxide film gets stabilized by high alkalinity developed, as the cement hydrates, diminishes slowly due the process of carbonation. Alkaline material reacts with the acidic solutions of carbon dioxide and sulphur dioxide formed in the atmosphere under moist conditions. These reactions reduce the alkalinity at and near the surface of the concrete. This process is known as carbonation. The process of carbonation causes a pH decrease from around 13 to around 8. Under this condition rebar passivity is no longer maintained and active corrosion initiates. Hence pH is a very appropriate parameter which reflects the state of matrix and the reinforcement in any cementitious composite. Since the corrosion inhibitors have to be used for the protection of the reinforcement, its effect on pH must be known before it is used in actual matrix. Keeping this in view, pH of solutions with different combinations containing various doses of corrosion inhibitors was determined.

4.4.1 TEST SCHEME

The pH values were determined for the solutions containing 1%, 3% and 5% of the corrosion inhibitors doses. Each solution was prepared using eight different systems. First four systems were potable water, potable water with 4% *NaCl*, potable water with cement slurry and potable water with cement slurry mixed with 4% *NaCl*. For the cement slurry a water cement ration of 0.7 was maintained. In the next four systems potable water was replaced with distilled water.

4.4.2 TEST RESULTS

For the determination of pH values, a digital pH-meter (No. 335 of Systronics Ltd., Ahmedabad, India) was used. The values of pH so determined are given in Table- 4.8.

4.4.3 DISCUSSIONS ON TEST RESULT

From the test results it has been observed that the addition of 4% *NaCl* both in potable water and the distilled water marginally decreases the pH. This observation has been found to be valid in all the systems. When the calcium nitrite inhibitor was added to the potable water, an increased value of pH was observed as compared to the blank potable water solution. With the increase in the calcium nitrite dose from 1% to 3% and further to 5%, an increase of 5.6% to 10.6 % in the pH value has been observed. Relatively a significant increase of 3.6% to 42.7% in pH value has been observed with the increase in the dose of calcium nitrite in distilled water solution. A decreasing trend in the value of pH has been observed with the increase of the dose of calcium nitrate from 1% to 3% and further to 5%. However, corresponding values of pH have been observed to be relatively lower when potable water was replaced with distilled water. The variation has been observed to be 3.3% to 6.9% in potable water and 0.4% to 16% in distilled water.

A reduction in the value of pH has been observed when the tannic acid was added to the potable water. However, this reduction is more in distilled water. A reduction of the order of 20.8% to 47.3% has been observed in the value of pH, when the dose of tannic acid was increased in potable water solution. Corresponding reduction in distilled water has been observed to be about 52.2% to 57.7%.

With the addition of calcium stearate, the pH value is found to be least affected in potable water, however a reduction of about 12.1% to 14.3% has been observed in the pH for saline water solution. With the increasing dose of calcium stearate the value of pH reduces marginally both in potable water and distilled water.

When the cement slurry was used as a solution medium, the effect of the dose of inhibitors on the pH value remains almost same as observed for earlier mediums.

Table- 4.8 pH Values for the Various Systems of Exposure

S. No.	System	pH Values							
		Potable water	Potable water + 4%NaCl	Potable water + Cement (Slurry)	Potable water + Cement (Slurry) + 4% NaCl	Distilled water	Distilled water + 4%NaCl	Distilled water + Cement (Slurry)	Distilled water + Cement (Slurry) + 4% NaCl
1.	Blank	7.53	7.40	12.22	12.14	7.26	7.04	12.18	12.14
2.	1% Calcium Nitrite	7.95	7.86	12.26	12.16	9.87	9.82	12.14	12.04
3.	3% Calcium Nitrite	8.25	8.17	12.26	12.16	10.20	9.98	12.17	12.04
4.	5% Calcium Nitrite	8.33	8.26	12.27	12.20	10.36	10.30	12.28	12.16
5.	1% Calcium Nitrate	7.28	7.23	12.12	12.08	7.23	7.13	12.25	12.00
6.	3% Calcium Nitrate	7.12	7.10	12.11	12.01	6.66	6.56	12.13	12.00
7.	5% Calcium Nitrate	7.01	6.96	12.03	11.93	6.23	6.28	12.08	11.87
8.	1% Tannic Acid	5.96	5.69	11.36	11.23	3.47	3.26	11.35	11.12
9.	3% Tannic Acid	4.43	4.22	11.08	10.97	3.18	3.00	10.85	10.69
10.	5% Tannic Acid	3.97	3.79	10.48	10.30	3.07	2.88	10.32	10.01
11.	1% Calcium Stearate	7.54	7.45	12.30	12.25	6.38	5.99	12.29	12.18
12.	3% Calcium Stearate	7.44	7.32	12.40	12.36	6.28	6.04	12.41	12.20
13.	5% Calcium Stearate	7.30	7.24	12.55	12.51	6.22	6.11	12.50	12.42

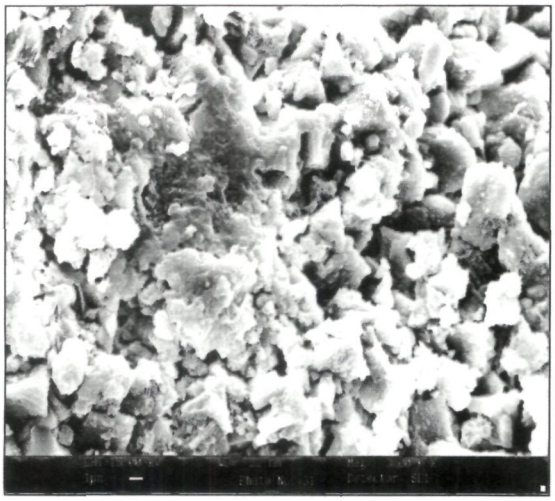
However, the value of pH rose to more than 12 in most of the cement slurry solution added with 1%, 3% and 5% dose of the corrosion inhibitors. Only for the tannic acid inhibited solution, a value of pH lower than 12 has been observed, however a small reduction of about 7% has been observed for 1% tannic acid solution. At higher doses of 3% and 5 %, the reduction is of the order of 9.3% to 14.2% in potable water and 11% to 15% in distilled water.

The value of pH indicates the nature of these chemicals whether they are acidic or alkaline in nature. With calcium nitrite inhibitor, the pH value increases whereas for calcium nitrate, tannic acid and calcium stearate there is a slight reduction in pH value. It is also worthwhile to mention here that the addition of these chemicals in cement slurry solution whether normal or saline remains highly alkaline (above 12) except for tannic acid where the pH value for 1% dose remains close to 12 but for higher doses reaches near 10.

4.5 SCANNING ELECTRON MICROSCOPE (SEM) INVESTIGATIONS

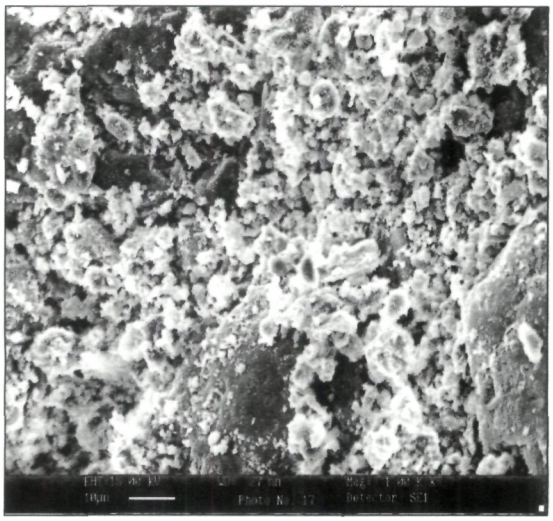
The microstructure of mortar particle plays an important role in determining its performance. The analysis of microstructure of mortar yields important information about the material with regard to particle size and orientation, phase identification, presence of voids *etc.* These details are used to determine the suitability of the material for the end use. This analysis becomes crucial when the material is subjected to aggressive environment.

For the Scanning Electron Microscope (SEM) analysis, samples were collected from the specimen crushed after compressive/tensile strength test. Small sized mortar pieces so collected were analyzed at two different magnifications. Samples were collected from both control and all the inhibited mortar. SEM analysis was carried out at Institute Instrumentation Centre, IIT, Roorkee, India. Images were captured at 1000X and 3000X magnification for each of the sample. The SEM images of the control and inhibited mortar specimens are shown in Figs. 4.13 and 4.14. For the potable water (control) specimen image, normal hydrated structure such as calcium silicate hydrate (*CSH*) gel, scattered crystallized calcium hydroxide and unfilled pores can be seen.

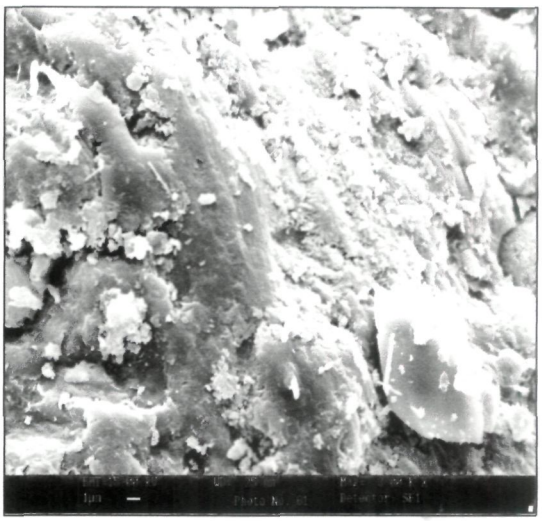


Control in Potable Water (3000X)

Control in Saline Water (3000X)



1% Calcium Nitrite (1000X)



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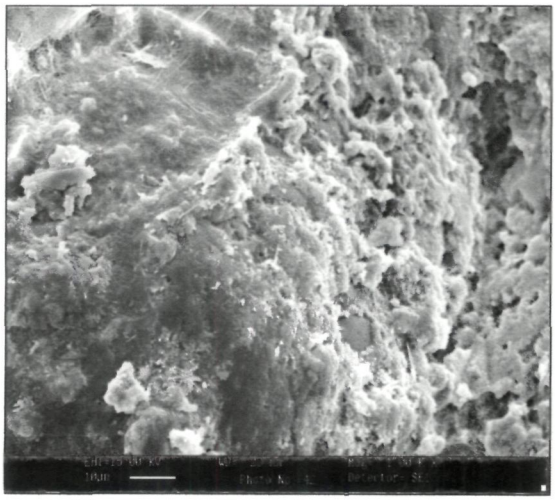

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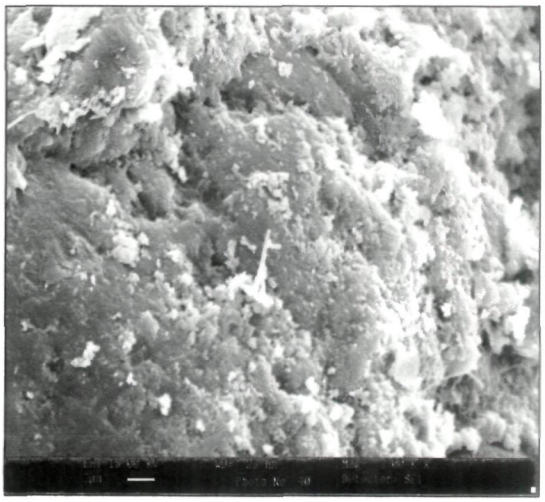
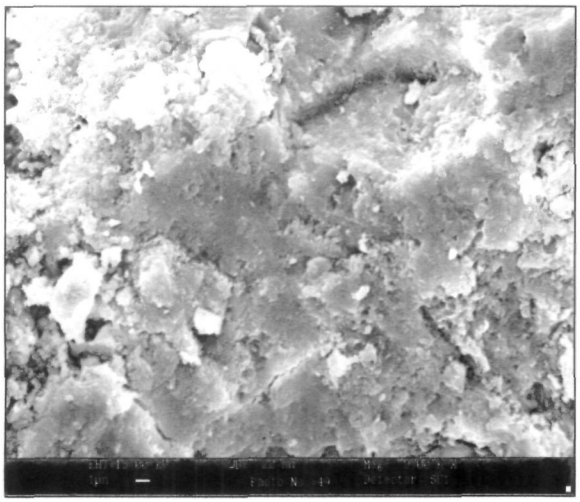
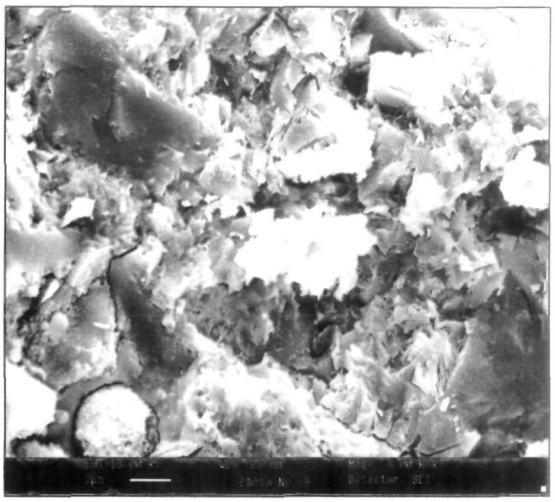


5% Calcium Nitrite (3000X)

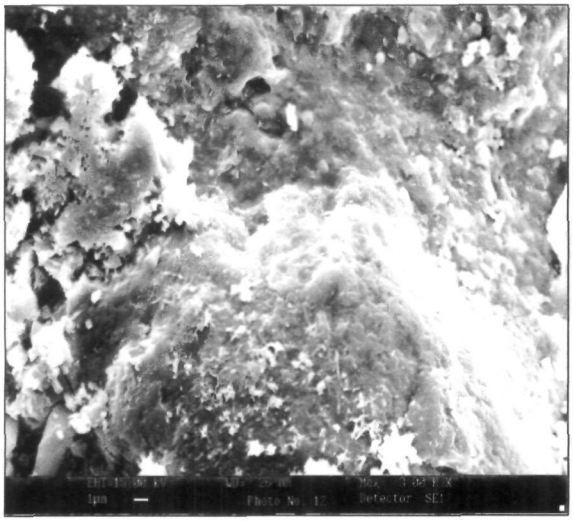
Fig 4.13 Scanning Electron Microscope (SEM) Images of Control and Calcium Nitrite Inhibited Mortar



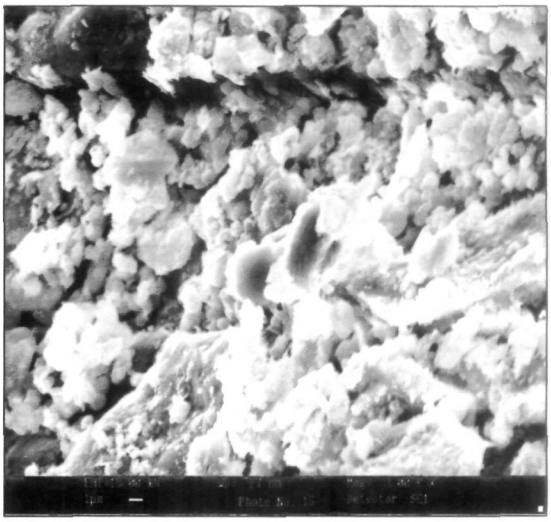
1% Calcium Nitrate (3000X)



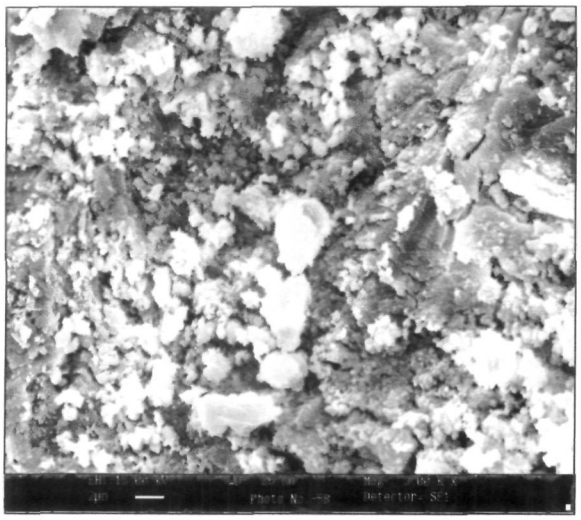
5% Calcium Nitrate (3000X)



1 % Tannic Acid (3000X)



5% Tannic Acid (3000X)



1% Calcium Stearate (3000X)

5% Calcium Stearate (3000X)

Fig 4.14 Scanning Electron Microscope (SEM) Images of Calcium Nitrate, Tannic Acid and Calcium Stearate Inhibited Mortar

However, for the control specimen in saline water, pores appear to be filled by sodium chloride crystals. It is difficult to speculate much about the texture and structure of the inhibited mortar. If the admixture is inert in nature then the gain in strength can be attributed to the lesser voids, as these are occupied by the particles of such material. But in the present situation, the chemical corrosion inhibitors may play a dual role as these occupy the voids and also, it can react with the constituents of cement. The increased density can increase the strength but at same time chemical reactions can add some strength or even reduce it, depending on its reaction with C_3S, C_2S and C_3A. Therefore, the level of packing and aggregate/material interface can be attributed to the increase or decrease in strength.

However, for all the inhibited mortar images lesser voids are seen as compared to the control images (Figs. 4.13 and 4.14). The particles can be seen as if though they are attached, stuck or they may be present with cross linking to each other. The surface appears to be much smoother as compared to that observed for the control specimens. Nevertheless, to arrive at more fruitful and meaningful conclusions, exhaustive studies are necessary which are beyond the scope of the present investigation.

4.6 ELECTROCHEMICAL STUDIES

Potentio-dynamic tests were undertaken to observe the effectiveness of the corrosion inhibitors. Polarisation resistance method and impedance measurements were used for the electrochemical analysis. Four different corrosion inhibitors namely calcium nitrite, calcium nitrate, tannic acid and calcium stearate, with the concentration level of 1% and 5% under two types of mediums namely potable water and saline water were used. Tests were conducted at Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India (CSIR Laboratory). Electrochemical System Model "Gill AC" (500 *mA*/ 100 *kHz*/ Guard Ring of ACM instruments, U.K.), was used for these experiments. The instrument had inbuilt software support to evaluate corrosion kinetic parameters. The details of the instrument are shown in Fig. 4.15.

A platinum foil was used as the auxiliary electrode, a saturated calomel electrode was used as reference electrode and mild steel was used as working electrode. The experiments were carried out at a constant temperature of 28±2 °C.

4.6.1 TEST SPECIMEN

Mild steel strips of 1 cm^2 exposed area were used as working electrode for this test as shown in Fig. 4.16. The working electrode was polished with 0/0, 1/0, 2/0, 3/0 and 4/0 emery papers successively and degreased with acetone.

4.6.2 POTENTIO-DYNAMIC POLARISATION STUDIES

Potentio-dynamic polarisation studies were undertaken using mild steel specimen shown in Fig. 4.16, in potable and saline water containing four different inhibitors keeping the dose of inhibitors as 1% and 5%. The objective of the test was to evaluate the corrosion parameters such as corrosion potential (E_{corr}), anodic Tafel slope (b_a), cathodic Tafel slope (b_c), corrosion current (I_{corr}), and corrosion rate. Two different test solutions were prepared using distilled water and potable water. A constant quantity of the test solution was taken in the polarisation cell. The working counter and reference electrodes were assembled and connections were made. A time interval of about 10–15 *minutes* was given for each system to attain a steady state. Both cathodic and anodic polarisation curves were recorded potentio-dynamically as shown in Figs. 4.17 – 4.34. The potentio-dynamic conditions correspond to a potential sweep rate of 1 mVs^{-1} and potential ranges of +200 mV to −200 mV from the OCP. All the experiments were carried out at constant temperature of 28±2°C. The corrosion kinetic parameters *viz.* E_{corr}, b_a, b_c I_{corr}, and corrosion rate are given in Table- 4.9.

4.6.3 A.C. IMPEDANCE MEASUREMENTS

The three-electrode cell assembly was used for A.C. impedance measurement also. The mild steel-working electrode was polished and degreased as before and immersed in the test solution taken in the cell. The reference and the platinum counter electrodes were assembled and connections were made. A time interval of 10–15 *minutes* was given for the OCP to reach a steady value. An alternating voltage of 20 mV was applied. Impedance measurements were carried out for various frequencies (0.1–30000Hz) using the same electrochemical measurement unit. Corrosion parameters were obtained using inbuilt equipment software support as mentioned earlier. The results of the impedance study are presented in Table- 4.10.

Fig. 4.15 Electrochemical Measurement Unit

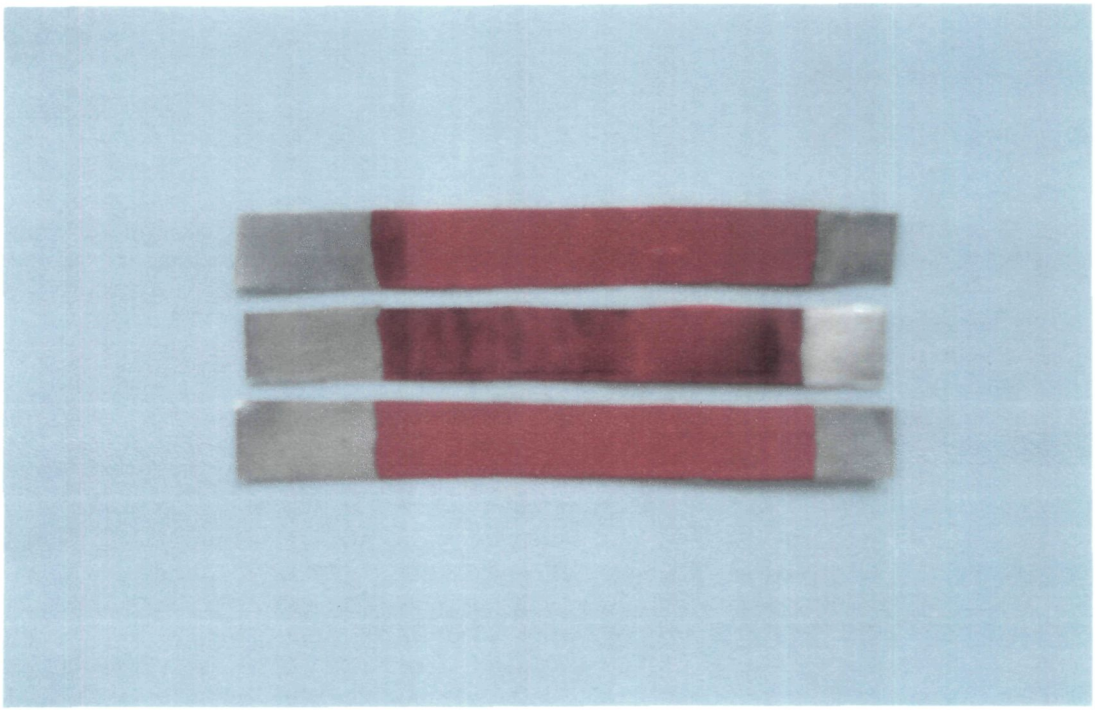


Fig. 4.16 Mild Steel Specimen Used as Working Electrode for the Electrochemical Study

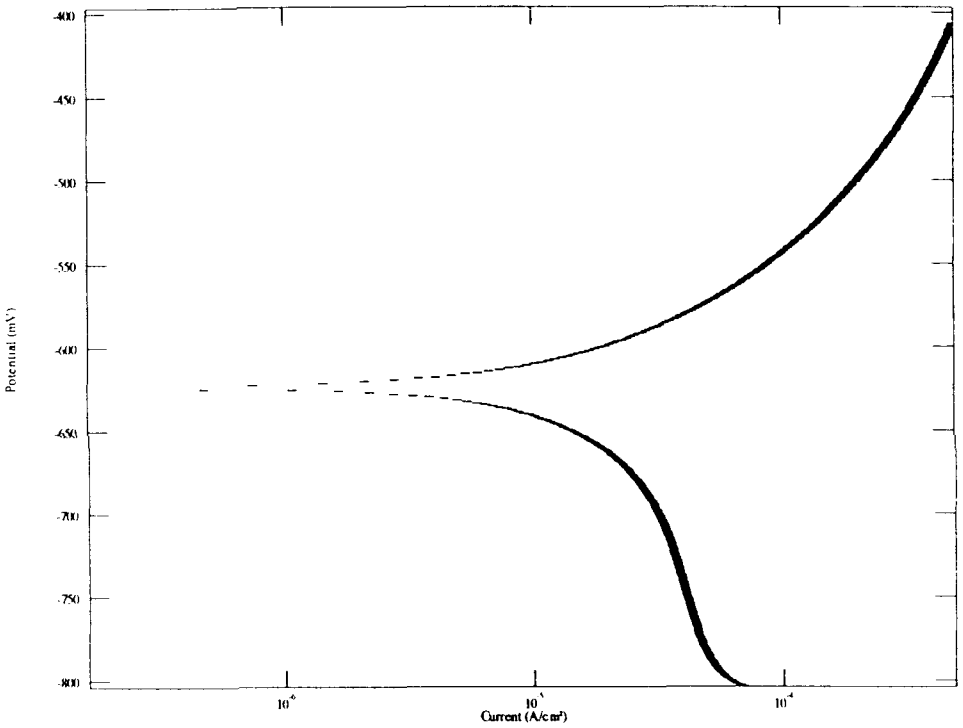


Fig. 4.17 Tafel Plot for Mild Steel Specimen in Potable Water (Blank-1)

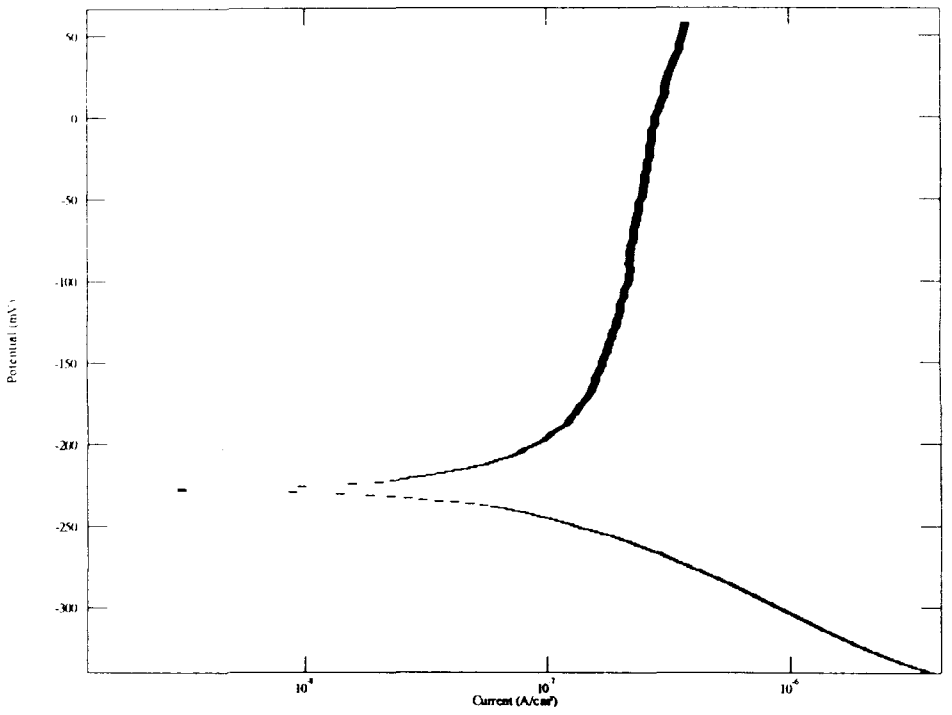


Fig. 4.18 Tafel Plot for Mild Steel Specimen with 1% Calcium Nitrite in Potable Water

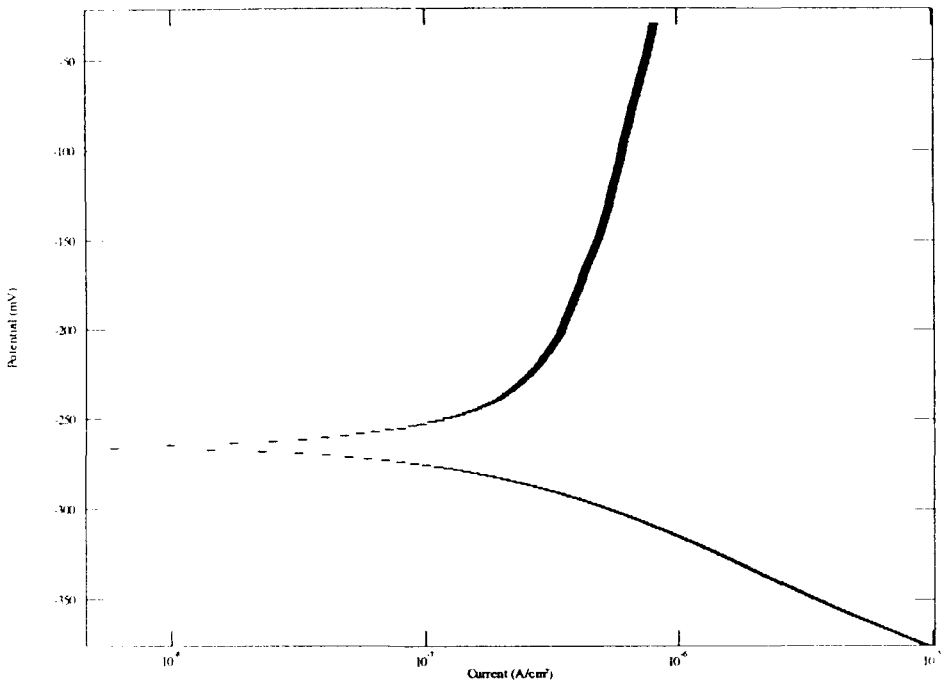


Fig. 4.19 Tafel Plot for Mild Steel Specimen with 5% Calcium Nitrite in Potable Water

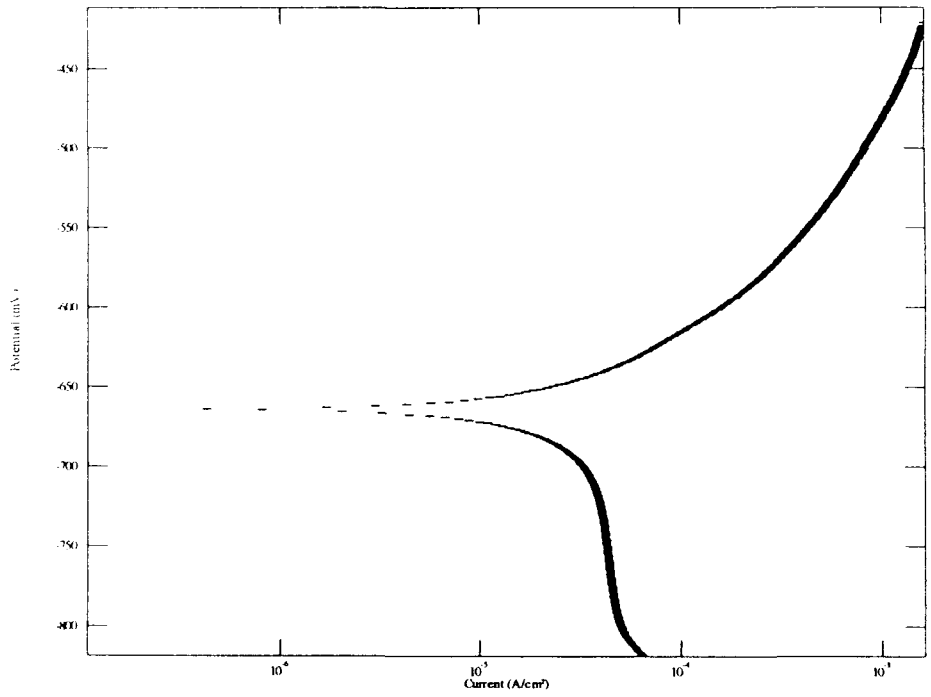


Fig. 4.20 Tafel Plot for Mild Steel Specimen with 1% Calcium Nitrate in Potable Water

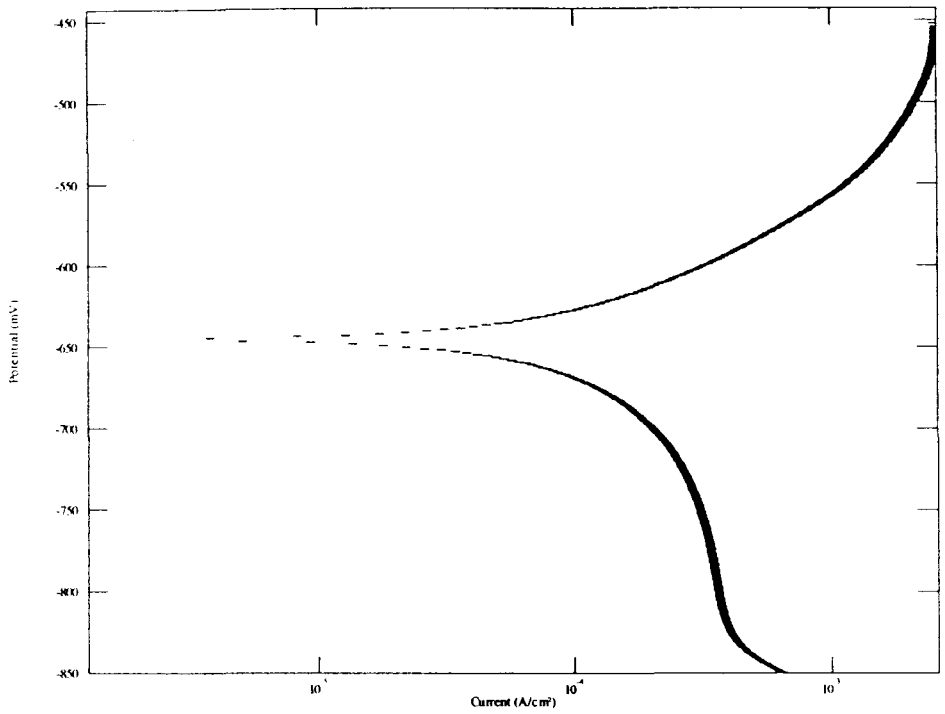


Fig. 4.21 **Tafel Plot for Mild Steel Specimen with 5% Calcium Nitrate in Potable Water**

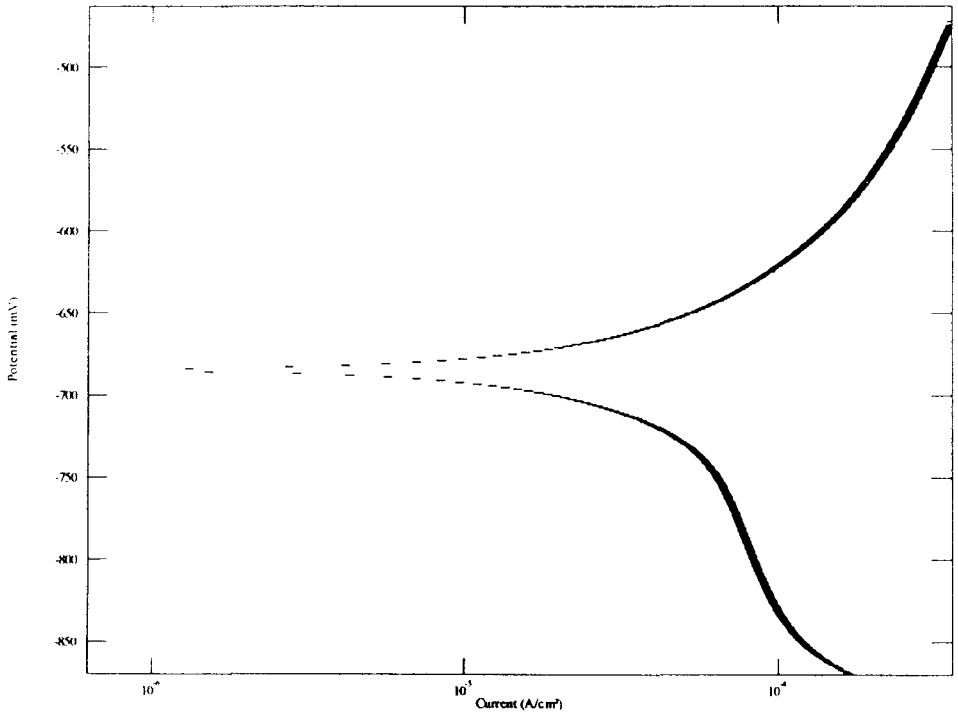


Fig. 4.22 **Tafel Plot for Mild Steel Specimen with 1% Tannic Acid in Potable Water**

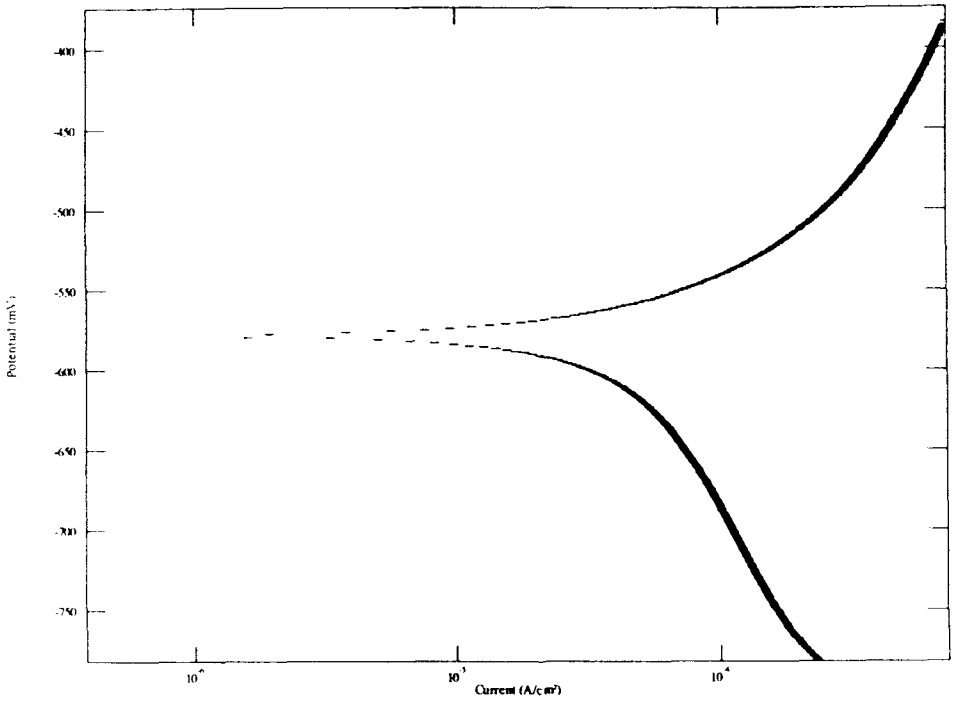


Fig. 4.23 Tafel Plot for Mild Steel Specimen with 5% Tannic Acid in Potable Water

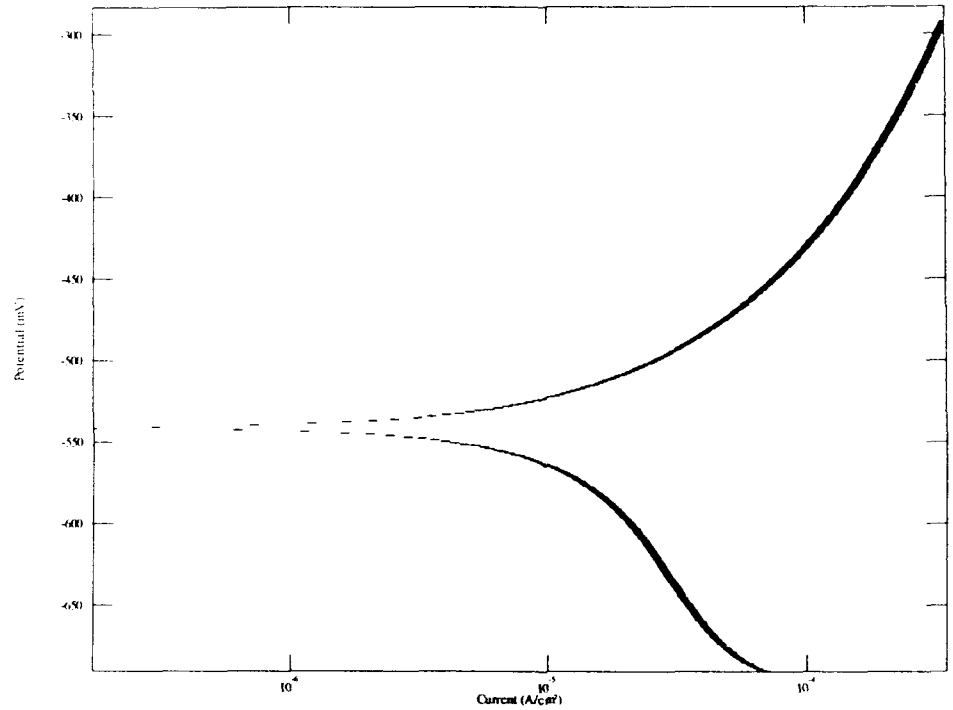


Fig. 4.24 Tafel Plot for Mild Steel Specimen with 1% Calcium Stearate in Potable Water

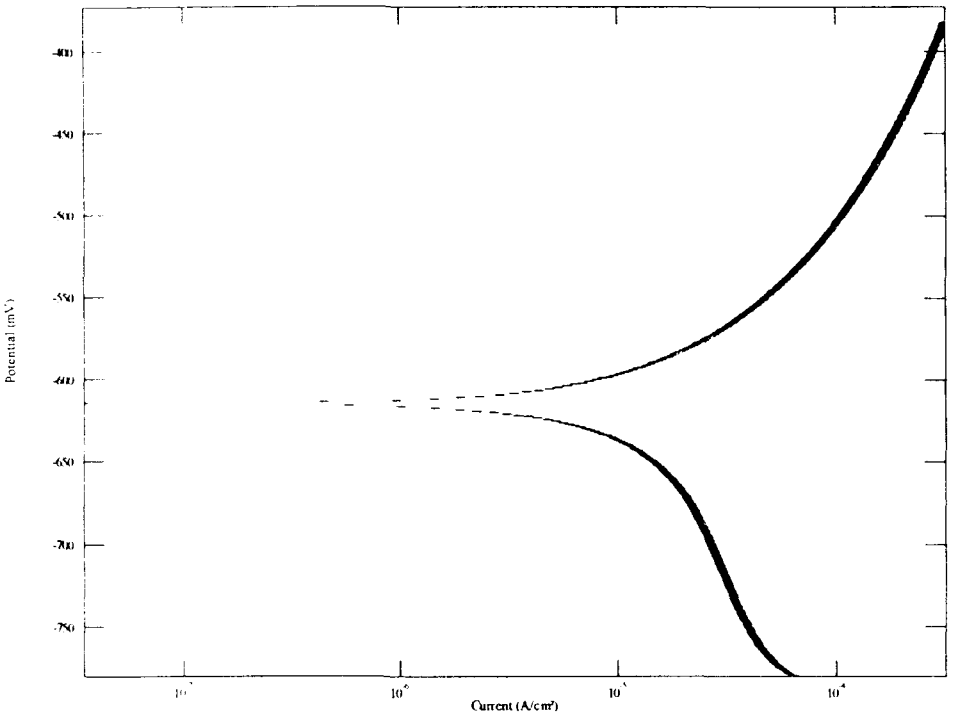


Fig. 4.25 Tafel Plot for Mild Steel Specimen with 5% Calcium Stearate in Potable Water

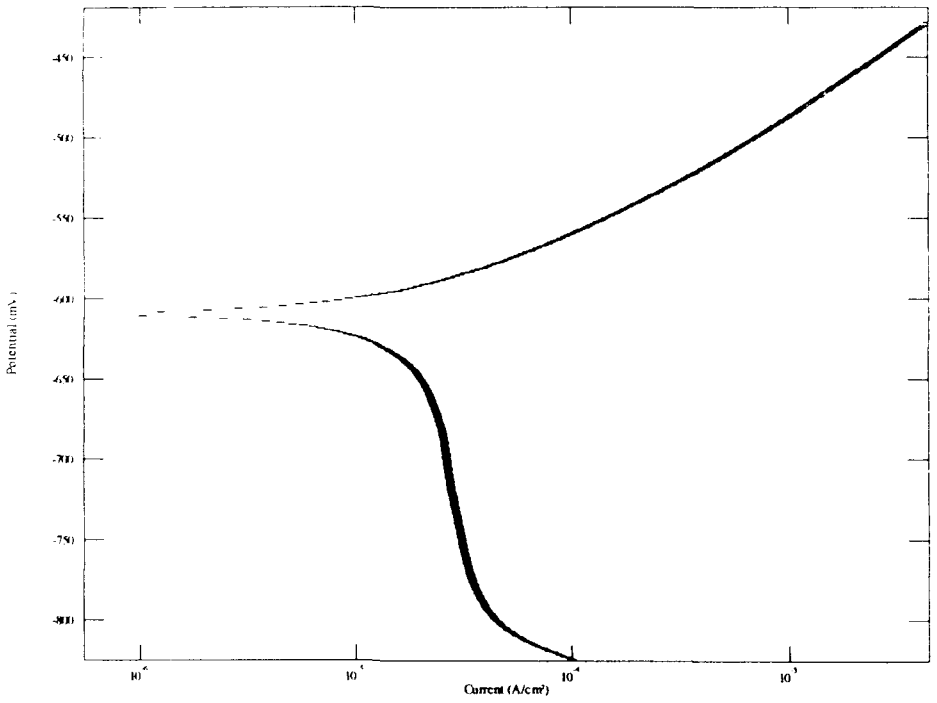


Fig. 4.26 Tafel Plot for Mild Steel Specimen in Saline water (4% *NaCl*) Blank-2

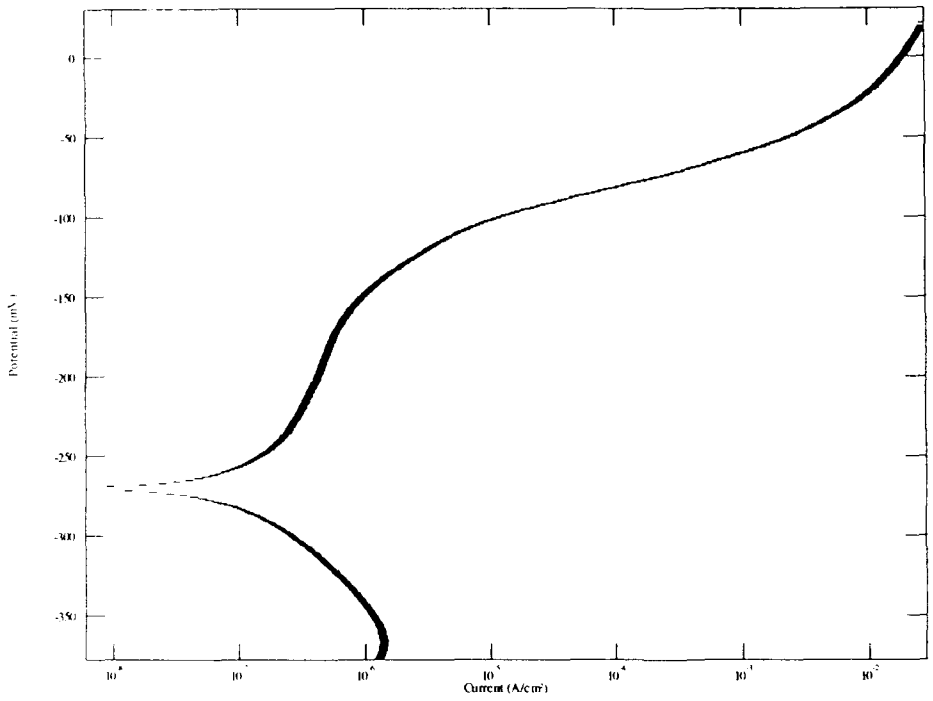


Fig. 4.27 Tafel Plot for Mild Steel Specimen in Saline water (4% *NaCl*) with 1% Calcium Nitrite

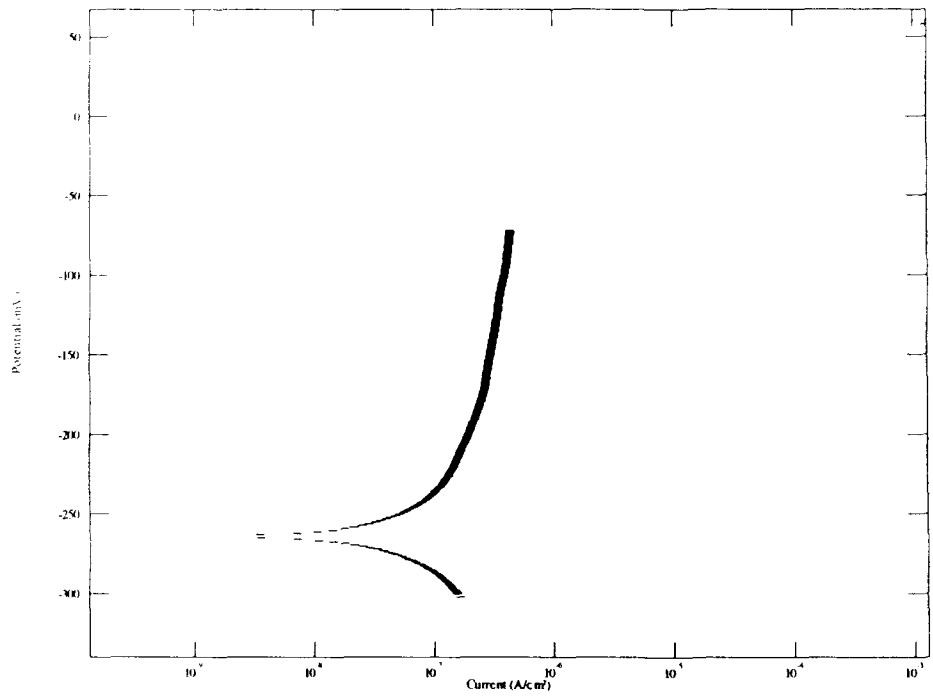


Fig. 4.28 Tafel Plot for Mild Steel Specimen in Saline water (4% *NaCl*) with 5% Calcium Nitrite

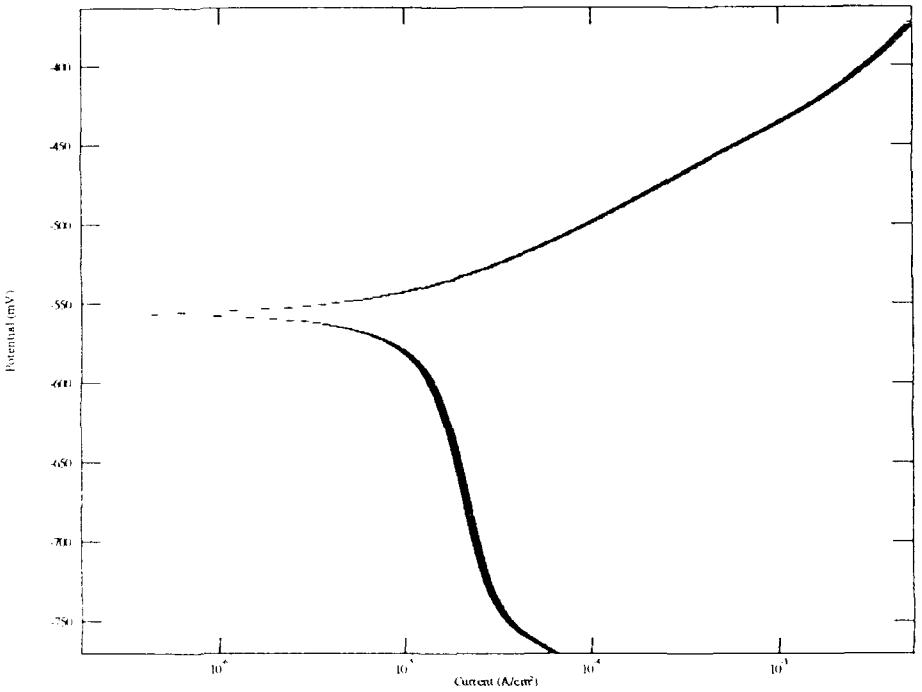


Fig. 4.29 **Tafel Plot for Mild Steel Specimen in Saline water (4% *NaCl*) with 1% Calcium Nitrate**

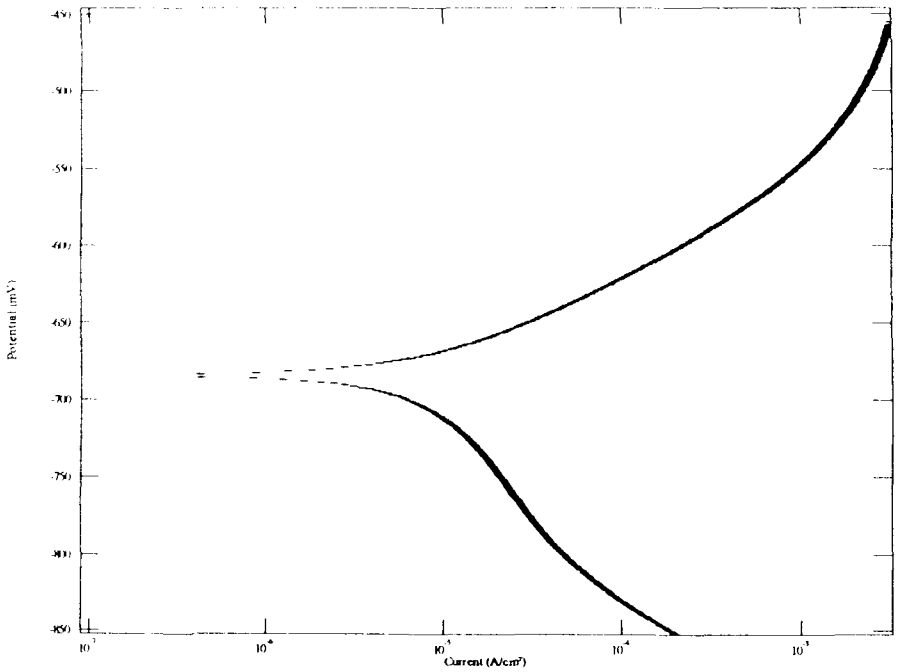


Fig. 4.30 **Tafel Plot for Mild Steel Specimen in Saline water (4% *NaCl*) with 5% Calcium Nitrate**

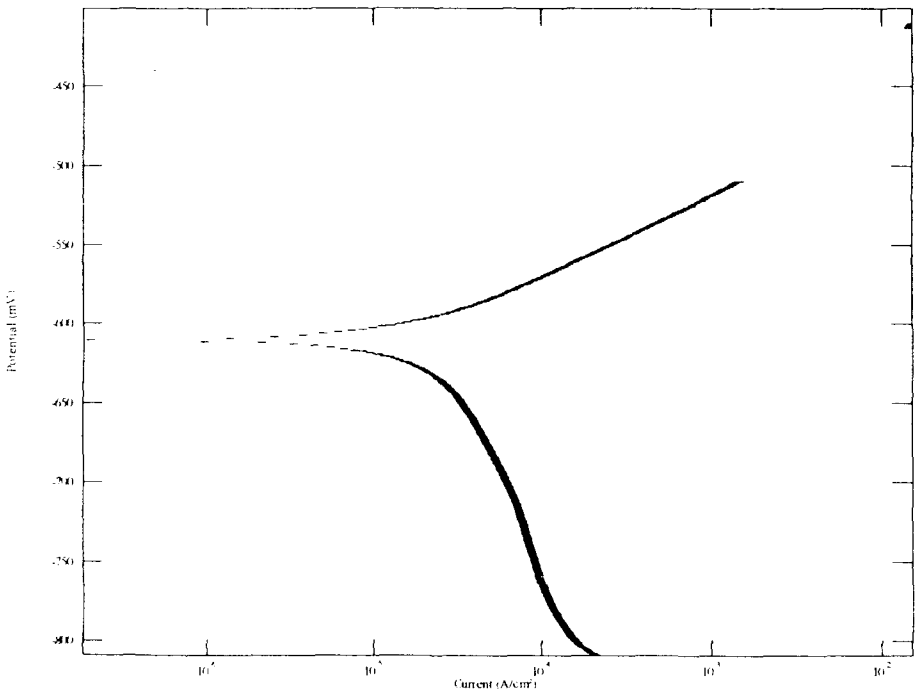


Fig. 4.31 **Tafel Plot for Mild Steel Specimen in Saline water (4% *NaCl*) with 1% Tannic Acid**

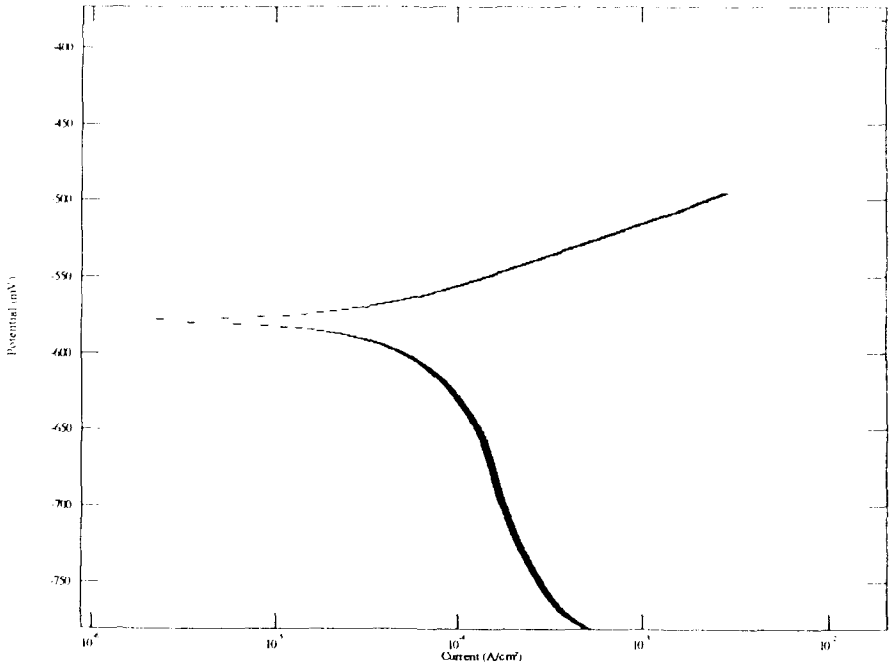


Fig. 4.32 **Tafel Plot for Mild Steel Specimen in Saline water (4% *NaCl*) with 5% Tannic Acid**

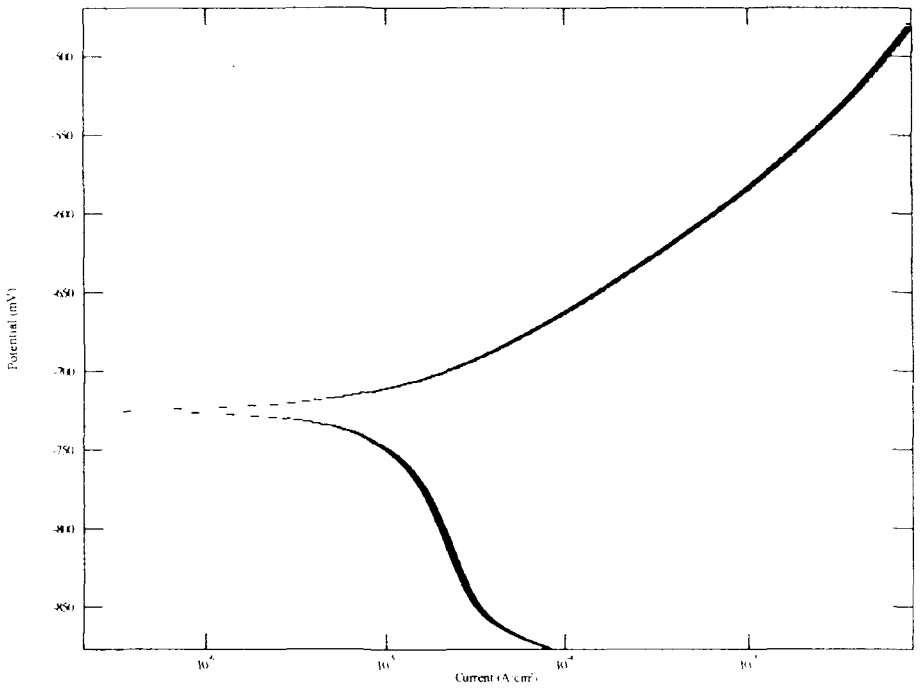


Fig. 4.33 Tafel Plot for Mild Steel Specimen in Saline water (4% *NaCl*) with 1% Calcium Stearate

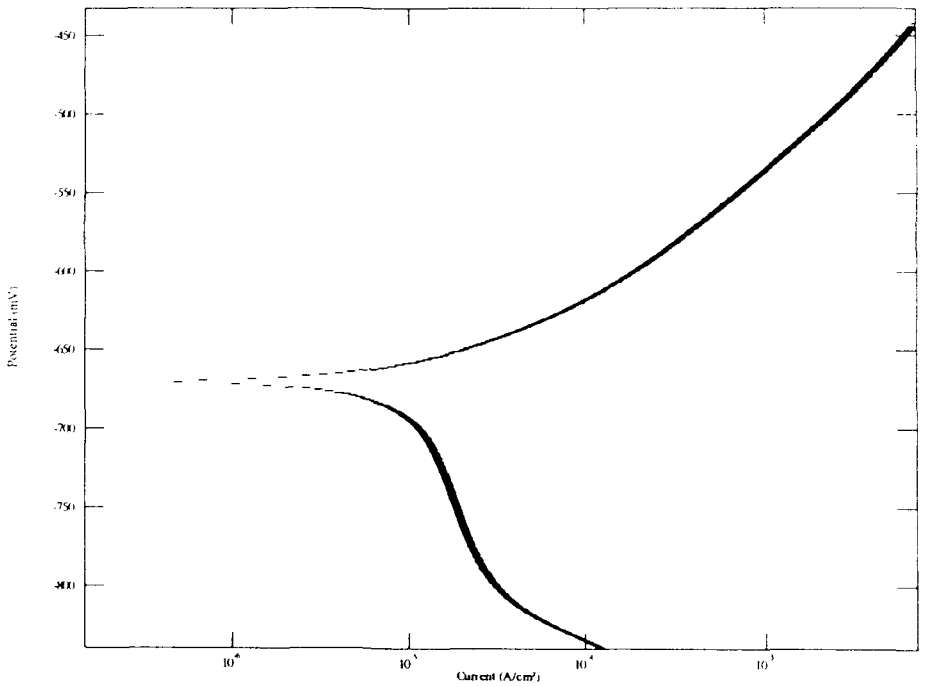


Fig. 4.34 Tafel Plot for Mild Steel Specimen in Saline water (4% *NaCl*) with 5% Calcium Stearate

Table 4.9 Results of Potentio-dynamic Study (Tafel Extrapolation)

OCP = ±200 *mV*; Sweep rate = 1 *mV/sec*

S. No.	System	E_{corr} (*mV*)	b_a (*mV*)	b_c (*mV*)	I_{corr} ($\mu A/cm^2$)	Corrosion Rate (*mpy*)
1.	Blank-1 (Potable Water)	-627	62	94	22.19000	10.1600
2.	1% Calcium Nitrite	-135	65	37	0.03334	0.0152
3.	5% Calcium Nitrite	-172	46	32	0.00030	0.0000
4.	1% Calcium Nitrate	-658	62	53	0.01500	6.7900
5.	5% Calcium Nitrate	-645	51	75	0.04600	21.1920
6.	1% Tannic Acid	-666	72	97	0.01800	8.2770
7.	5% Tannic Acid	-577	44	69	0.01400	6.7050
8.	1% Calcium Stearate	-542	55	81	0.01390	6.3530
9.	5% Calcium Stearate	-575	51	69	0.00429	1.9591
10.	Blank-2 (Saline Water)	-609	54	164	94.86000	43.2850
11.	1% Calcium Nitrite	-173	45	80	0.34000	0.0386
12.	5% Calcium Nitrite	-158	34	22	0.28600	0.0076
13.	1% Calcium Nitrate	-566	146	30	4.14700	1.8920
14.	5% Calcium Nitrate	-679	38	65	4.02700	1.8380
15.	1% Tannic Acid	-611	59	238	0.57721	3.9230
16.	5% Tannic Acid	-575	34	62	24.50000	11.1830
17.	1% Calcium Stearate	-672	42	79	4.85900	2.2170
18.	5% Calcium Stearate	-635	31	121	5.31400	2.4250

Table 4.10 Results of Impedance Study

Frequency range = 0.1 *Hz* – 30,000 *Hz*; Current = 20 *mV* AC

S. No.	System	E_{corr} (*mV*)	R_s (*Ohm cm*^{2})	R_{ct} (*Ohm cm*^{2})	C_{dl} $\mu F/cm^2$	I_{corr} ($\mu A/cm^2$)	Corrosion Rate (*mpy*)
1.	Blank-1 (Potable Water)	-475	317	475	20.600	54.850	25.0300
2.	1% Calcium Nitrite	-160	5004	23830	0.136	1.095	0.4995
3.	5% Calcium Nitrite	-196	2731	12330	0.065	0.000	0.0000
4.	1% Calcium Nitrate	-527	108	295	38.850	88.280	40.2800
5.	5% Calcium Nitrate	-522	56	83	984.600	314.500	143.5000
6.	1% Tannic Acid	-564	228	271	74.200	96.050	43.8300
7.	5% Tannic Acid	-524	259	134	15.380	194.000	88.5000
8.	1% Calcium Stearate	-403	732	1317	6.222	19.810	9.0380
9.	5% Calcium Stearate	-315	4.185×10^{7}	1.001×10^{8}	9.0447×10^{-4}	0.026	1.19×10^{-5}
10.	Blank-2 (Saline Water)	-610	121	411	80.510	63.360	28.9100
11.	1% Calcium Nitrite	-230	740	10140	0.277	2.573	1.1740
12.	5% Calcium Nitrite	-208	6917	17700	0.045	1.474	0.6725
13.	1% Calcium Nitrate	-493	297	324	338.600	80.320	36.6500
14.	5% Calcium Nitrate	-543	51	27	26.460	943.100	330.3000
15.	1% Tannic Acid	-582	26300	80580	10.190	0.324	0.1477
16.	5% Tannic Acid	-570	100	109	90.340	238.900	109.0000
17.	1% Calcium Stearate	-564	421	8879	0.502	2.938	0.0341
18.	5% Calcium Stearate	-494	74940	8689	0.218	3.002	0.0348

4.6.4 DISCUSSION ON ELECTROCHEMICAL RESULTS

The corrosion kinetic parameters *viz.* corrosion potential (E_{corr}), anodic Tafel slope (b_a), cathodic Tafel slope (b_c), corrosion current (I_{corr}), and corrosion rate from Tafel extrapolation (Table- 4.9) and E_{corr}, R_s, R_{ct}, C_{dl}, I_{corr} and corrosion rate from Impedance study (Table- 4.10) were obtained. These parameters indicate the level of the inhibition exhibited by the respective corrosion inhibitors. The values of these parameters obtained for the specimen in various solution systems are compared with the values found for the specimen in plain potable water without any inhibitor (Blank-1), and in saline water (Blank-2). Potential quoted in the electrochemical results are referred to the saturated calomel electrode (*SCE*). Comparisons wherever made are with the Blank-1 when potable water is used as a medium and with the Blank-2 when saline water is used as a medium.

4.6.4.1 TAFEL EXTRAPOLATION

The effect of various parameters on corrosion kinetic parameters is discussed below. The Tafel plots have been given in Figs. 4.17 – 4.34 and the results have been presented in Table- 4.9.

Corrosion Potential (E_{corr})

For calcium nitrite inhibited solution prepared using potable water, it has been observed that the corrosion potential shifts to a remarkably less negative value (about one fourth of the value obtained for blank specimen). However, for calcium nitrate and calcium stearate inhibited solutions a marginal shift to the more negative value has been observed. Comparatively, the highest negative shift has been observed for the solution containing 1% tannic acid. The shift to more negative values is marginal for 5% tannic acid solution.

In saline water solution, shift to lesser negative value has been obtained for both the doses of calcium nitrite solution. In this case also, the corrosion potential shifts to a remarkably less negative value (about one fourth of the value obtained for Blank-2). For calcium nitrate solutions, a marginal shift to less negative value for 1% inhibitor dose solution and a more negative value for 5% inhibitor dose solution have been observed. For the observations made in 1% tannic acid solution, corrosion potential value is almost identical to the Blank-2 solution.

However, for 5% tannic acid a nominal shift towards a lesser negative value has been observed. A more negative shift has been observed for both the doses of calcium stearate. However shift is more for 1% dose and less for 5% dose.

Corrosion Current Density (I_{corr})

While comparing the values obtained in potable water system containing corrosion inhibitors, corrosion current densities were found to reduce to an extremely lower value as compared to Blank-1, indicating the effectiveness of all the systems in controlling the corrosion. For calcium nitrite, tannic acid and calcium stearate, lowering of cathodic current densities is more pronounced with higher inhibitor dose. However, for calcium nitrate, nominal increase of I_{corr} has been observed as the dose of the inhibitors is increased from 1 to 5%.

As expected, in saline water systems (Blank-2) a higher value of the I_{corr} than the corresponding value of the potable water system (Blank-1) has been observed. For the inhibited systems, calcium nitrite here also gives the best results as the I_{corr} values are extremely low for both the doses. For the solutions containing 1% and 5% of calcium nitrate and calcium stearate, almost similar values of I_{corr}, substantially lower than the Blank-2, have been observed. For the tannic acid solution, a reduced value of I_{corr} has been observed for both the doses. The reduction for 1% tannic acid solution has been comparable to the calcium nitrite values, however, a relatively higher value of I_{corr} has been found for 5% tannic acid solution which may be attributed to the lower pH value of the solution.

Corrosion rate

When potable water is used, for all the inhibitors the corrosion rate lower than the Blank-1 has been observed for all the systems except for the 5% dose of calcium nitrate. The lowest corrosion rate has been observed for calcium nitrite. The corrosion rate values are found to be marginally different in each case. An appreciably lower value of corrosion rate has been observed for 5% calcium stearate. For 1% dose of the calcium nitrate and calcium stearate, values lower by 35% than Blank-1 have been observed. For tannic acid the corrosion rate has been found to be lower by 18.6% and 34% respectively for 1% and 5% dose.

Corrosion rate for Blank-2 has been found to be higher than the Blank-1 value however much better and consistent results have been observed for the inhibited saline water systems. In this system also, best result has been observed for the calcium nitrite inhibited solution. For the system inhibited with calcium nitrate and calcium stearate, a remarkably lower value has been observed for both the doses. For tannic acid inhibited solution an appreciably lower value of corrosion rate has been observed for 1% solution and a relatively higher value has been found for 5% solution. Interestingly, both these values are much lower than the Blank-2 value.

A marked shift of E_{corr} to a less negative value and also the anodic curve to very low current densities, suggests that the calcium nitrite is an anodic inhibitor. Looking upon the amount of such shift for other inhibitors it can be concluded that these behaved as mixed inhibitors. In line with the results reported in literature, calcium nitrite showed extremely high inhibition. Other three inhibitors *viz.* calcium nitrate, tannic acid, calcium stearate have also shown acceptable inhibition. In a few cases inconsistent values were also obtained.

4.6.4.2 A.C. IMPEDANCE

Evaluation of corrosion kinetic parameters by AC-impedance technique in potable and saline water systems has been presented in Table- 4.10. The comparisons are made with Blank-1 when potable water is used as a medium and with the Blank-2 when saline water is used as a medium.

Corrosion potential (E_{corr})

As far as corrosion potential values are concerned, almost exactly similar pattern as that obtained in Tafel extrapolation has been found here also. The values for the calcium nitrite inhibitor showed shift towards a lesser negative value both in potable and saline water than Blank-1 and Blank-2 respectively. In potable water system, calcium nitrate and tannic acid exhibited a shift to a more negative value, however, shift towards a less negative value has been observed for calcium stearate. In the saline water systems, the values for all the inhibitors remain on to less negative side.

R_{ct} and C_{dl}

It is a well known fact that a good inhibited system must show a grater R_{ct} and lower C_{dl} values when compared to the respective blank system (Murlidharan *et al.*, 2004). A much higher value of R_{ct} and an extremely low value of C_{dl} has been observed for the calcium nitrite both in potable and saline water system which clearly indicates a very good inhibition. Almost similar trend has been observed for 1% and 5% dose of calcium stearate. A remarkably higher R_{ct} value along with fairly low value of C_{dl} is observed for 1% tannic acid solution in saline water condition. The results obtained for 5% tannic acid solution and for the solution containing 1% and 5% dose of calcium nitrate have not shown any sign of inhibition.

Corrosion Current Density (I_{corr})

Similar pattern of result as explained for R_{ct} and C_{dl} values has been observed for corrosion current density. Lower current density has been observed for calcium nitrite and calcium stearate in both the potable and saline water medium. The reduction of the limiting current density can be related to the adsorption of the inhibitor on the metal surface. However, a higher value of I_{corr} has been noticed for other inhibitors except for 1% tannic acid in saline water system.

Corrosion Rate

A very low corrosion rate indicates a very high inhibition for the calcium nitrite inhibited system. Almost same level of inhibition has been found in both potable and saline water system. Calcium stearate also indicated very low corrosion rate both in potable and saline water medium. Except for 1% tannic acid, a corrosion rate higher than the blank system has been observed for 5% tannic acid and also for 1% and 5% calcium nitrate system.

4.7 CONCLUDING REMARKS

In this chapter an attempt has been made to study the effect of four corrosion inhibitors as mentioned earlier, on the setting time of cement, compressive and tensile strength of cement-sand mortar, pH value of different exposure mediums and some corrosion kinetic electrochemical parameters.

It has been observed that most of the inhibitors acted as an accelerator to the initial and final setting of the cement, though the rate of acceleration was different in each case. However, it is interesting to note that at higher doses some of the inhibitors (5% calcium nitrite and tannic acid) behaved as retarder. This observation is in line with the findings reported by Mehta (1986). It is important to mention here that irrespective of the inhibitors acting as accelerator or as retarder, the values of the initial and final setting time are within the recommended limits of the relevant code of practice.

A usual increase in compressive and tensile strength with age has been observed for the control, saline and most of the mortar mixes having different percentages of the corrosion inhibitors. A marginally lower value of compressive strength has been noticed for cubes cured in saline water as compared to the control specimen cured in potable water. In some of the cases it has been observed that the early gain in strength was much lower than the control specimen. This observation was especially made for the specimens containing 3% and 5% dose of tannic acid and calcium stearate. Slow gain in strength at early age in some of the combinations can be attributed to the slow down of the reaction of C_3S by the addition of these chemicals in high concentration. A significant increase in strength after 28 *days* has been observed in a few of the other combinations, especially for calcium nitrate, which is perhaps due to the fact that the C_3S reaction gains momentum after 28 *days*. These chemicals might be acting as a catalyst to the C_2S reaction too, which also contributes to the gain in delayed strength.

The observed pH values indicate the nature of the inhibitors whether they are acidic or alkaline. With calcium nitrite inhibitor, the pH value increases whereas for calcium nitrate, tannic acid and calcium stearate there is a slight reduction in pH value. It is also important to mention here that when these inhibitors are used in cement slurry solution whether normal or saline, the pH value continues to be above 12 except for tannic acid where the pH value for 1% tannic acid dose remains close to 12 but reduces to 10 at 3% and 5% dose.

The electrochemical Tafel extrapolation and AC-impedance technique were applied to study the corrosion as well as electrochemical activity at the mild steel interface with and without the protective treatments. Calcium nitrite showed much better performance than the other three inhibitors in all the systems.

The calcium nitrate did not perform well as compared to other inhibitors. As far as organic inhibitors are concerned, in some cases calcium stearate has shown better results whereas in some of the conditions tannic acid has exhibited better performance.

Since the future scheme of investigations involved enormous amount of experimental tests on ferrocement cuboids and plates, it was not feasible to continue with the all four corrosion inhibitors. A better strategy was to choose the two best suited inhibitors one from inorganic set, comprising of calcium nitrite and calcium nitrate; and another from organic set, comprising of tannic acid and calcium stearate. On the basis of the better performance, ease in application and cost effectiveness, calcium nitrite and tannic acid were finally chosen as the best in-organic and organic inhibitors respectively for further studies. Apart from these advantages it is important here to mention that tannic acid inhibitor comes from the class of green inhibitors.

Calcium nitrate was dropped from the scheme of cuboid and plate investigations although it showed good sign of delayed strength but its electrochemical results were not so encouraging. Calcium stearate was not chosen because of its low solubility in water; nevertheless, it also showed good signs of inhibition.

The cost effectiveness behind tannic acid is largely due to its coverage action. A very small amount of tannic acid can form a protective film of iron tannate over a very large surface area of reinforcement. One of the reasons behind tannic acid being not so impressive is perhaps that it requires some time to form a protective film on to the surface of the metal. In electrochemical test no such time was available, as the test is started within 10-15 *minutes* after immersion of the specimen into the solution.

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Chapter 5

Tests on Mild Steel Plate, Naked and Slurry Coated Wire Mesh

5.1 GENERAL

The results of the first stage of study dealing with the selection of corrosion inhibitors for the improvement in durability of ferrocement have already been presented in the Chapter-4. Based on their performance, ease in use and cost effectiveness, two corrosion inhibitors namely calcium nitrite (henceforth referred as Type–I) and tannic acid (henceforth referred as Type–II) were selected for further studies. In the present chapter, the second stage of study, mainly aimed at evaluating the effectiveness of these inhibitors in controlling the corrosion under direct exposure condition has been presented. Gravimetric weight loss method has been used for the assessment of extent of corrosion in mild steel plates, steel wire meshes and slurry coated wire mesh specimens. It is important to mention here that the electrochemical tests were conducted on mild steel strips; hence the same were also included in the gravimetric weight loss method tests along with the steel wire meshes. This provided a better comparison with regard to efficiency of the corrosion inhibitors and thereby providing a better verification of test results. The weight loss, the efficiency of corrosion inhibitors, corrosion rate and penetration rate were the main parameters under investigation.

5.2 INVESTIGATION SCHEME AND TEST SPECIMENS

A total of six exposure mediums namely potable water (normal tap water), potable water with calcium nitrite (Type–I) and Tannic acid (Type–II) inhibitors; and artificial saline water (distilled water mixed with 4% *NaCl*), saline water with Type–I and Type–II inhibitors were undertaken for the present investigation.

The concentration of *NaCl* for the artificial saline water was kept as 4% which is very near to the sea water *NaCl* content. The exposure time was 30, 90, 180 and 360 *days* at room temperature. The doses of Type–I and Type–II inhibitors were kept as 1%, 3% and 5%. The details of the experimental scheme for the immersion test are shown in Table– 5.1. As explained in the previous section, three different types of test specimens *viz.* mild steel plate, welded steel mesh and slurry coated welded steel mesh were prepared for the study. The details of these specimens are given in Table– 5.2 and Figs. 5.1–5.3. For each exposure medium, the specimens were used in triplicate.

5.3 APPLICATION OF CORROSION INHIBITORS

For this stage of study the two corrosion inhibitors *viz.* calcium nitrite (Type- I) and tannic acid (Type- II) were used in different ways. Calcium nitrite inhibitor was directly dissolved in the medium for the mild steel plate specimen and naked steel wire mesh specimen. However, for the slurry coated specimen, calcium nitrite was added in cement slurry and a coating of this slurry was applied. Tannic acid was applied as a film over the surface of the specimen in all the three types of specimens wherein the specimens were dipped for 30 *minutes* in the solution of tannic acid, thereafter left, in open for air drying. After another 10 *minutes* or so, a thin film over the surface of the specimen becomes visible. Once the film formed over the surface of the specimen dries up, the mild steel plate and welded mild steel wire mesh specimens were exposed in potable or saline medium. The slurry coated specimen was prepared by applying coating of cement slurry over the tannic acid film. Mild steel plate and wire mesh specimens having films of tannic acid are shown in Fig. 5.4. Concentration of the inhibitor was taken by the weight of the medium.

5.4 TEST PROCEDURE

The specimens were prepared, cleaned, degreased and dried as per the recommendations of ASTM G1–03 and G31–72. Initial weight of the specimen was recorded using a digital electronic balance (Precisa–XB220A, Swiss Make) having a least count of 0.1 *mg*. Specimens were exposed to different mediums as explained in Table– 5.1. After the specified time of exposure, the specimens were taken out of the medium and cleaned as per the recommendations of ASTM G1–03, Annexure–A1.

After the specimen dries up, once again the weight of the specimen was recorded and the weight loss was noted. An average weight loss has been finally reported for each set of specimens, since the difference in the weight of the specimens was found to be negligible.

Table- 5.1 Investigation Scheme for Immersion Test

Exposure Medium	Dose of Inhibitor (%)	Designation of Exposure Medium	Duration of Exposure (*days*)
Potable Water (Blank-1)	0	NW	30, 90, 180 and 360
Potable Water with Inhibitor Type-I	1	NW I-1	30, 90, 180 and 360
	3	NW I-3	30, 90, 180 and 360
	5	NW I-5	30, 90, 180 and 360
Potable Water with Inhibitor Type-II	1	NW II-1	30, 90, 180 and 360
	3	NW II-3	30, 90, 180 and 360
	5	NW II-5	30, 90, 180 and 360
Saline Water (Blank-2)	0	SW	30, 90, 180 and 360
Saline Water with Inhibitor Type-I	1	SW I-1	30, 90, 180 and 360
	3	SW I-3	30, 90, 180 and 360
	5	SW I-5	30, 90, 180 and 360
Saline Water with Inhibitor Type-II	1	SW II-1	30, 90, 180 and 360
	3	SW II-3	30, 90, 180 and 360
	5	SW II-5	30, 90, 180 and 360

Table- 5.2 Details of Specimens for Immersion Test

Specimen Type	Size and Details
Mild Steel Plate	25×18.75×0.25 *mm*
Welded Steel Wire Mesh	Size of the Specimen = 32×32 *mm* Diameter = 1.42 *mm* Opening Size = 16 *mm*
Cement Slurry Coated Welded Steel Wire Mesh	Size of the Specimen = 32×32 *mm* Diameter = 1.42 *mm* Opening Size = 16 *mm*

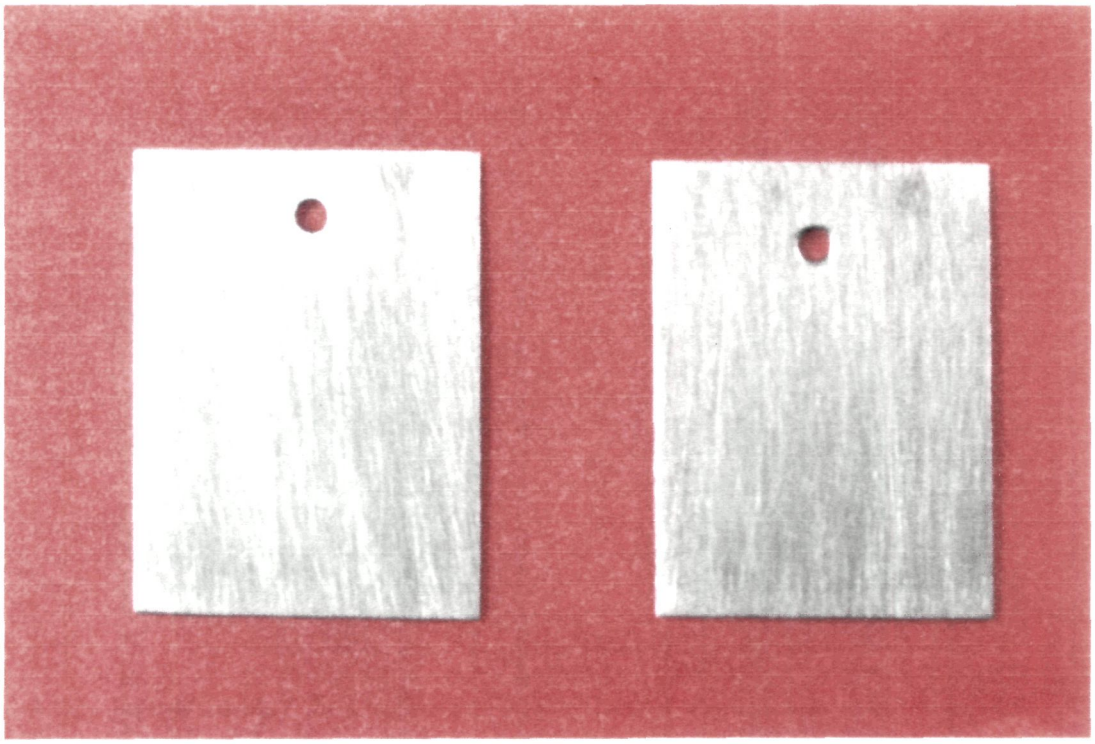


Fig. 5.1 Mild Steel Plate Specimens

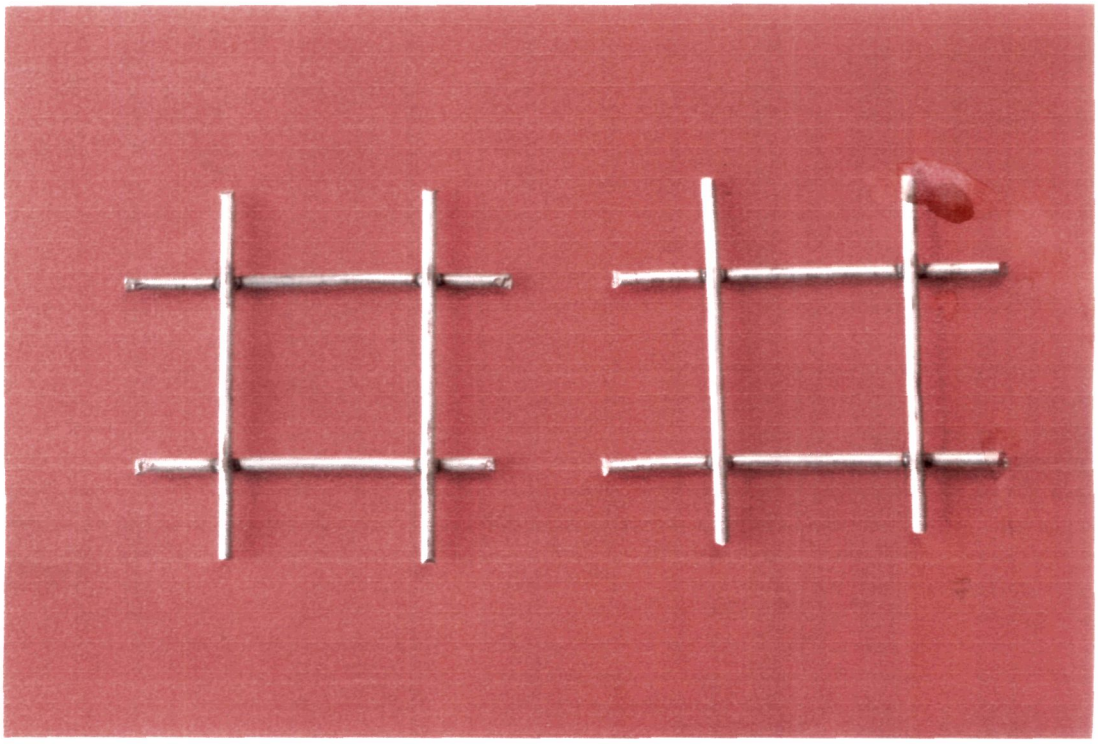


Fig. 5.2 Naked Welded Steel Wire Mesh Specimens

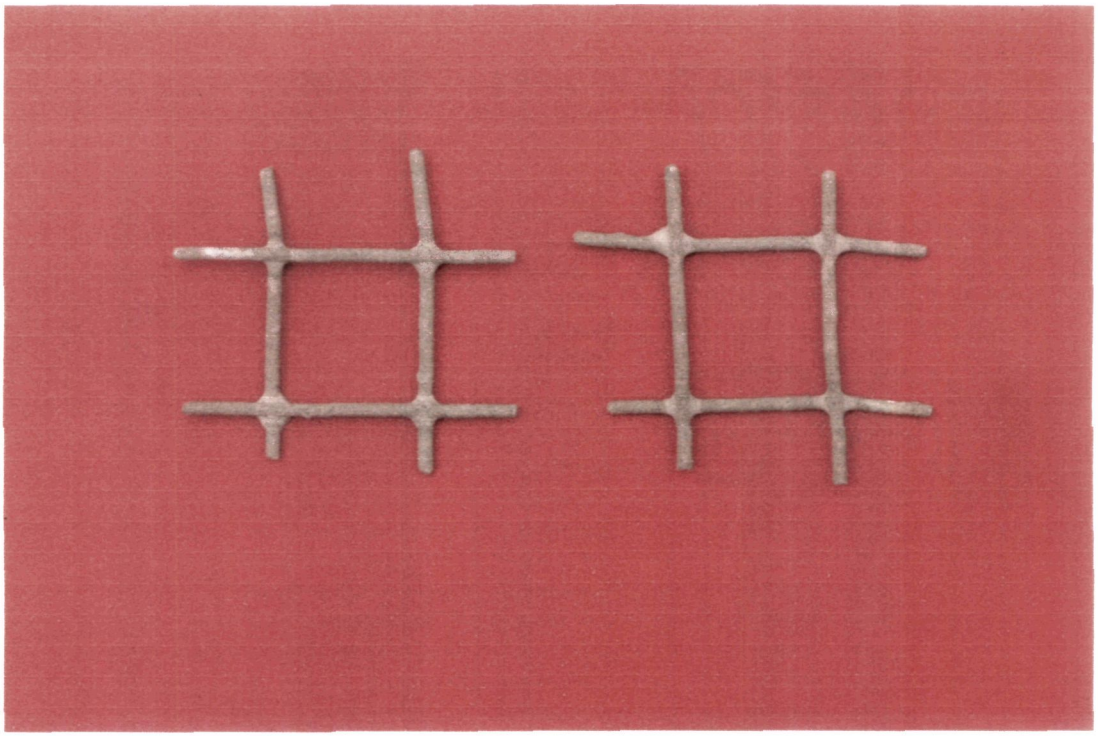


Fig. 5.3 Cement Slurry Coated Welded Steel Wire Mesh Specimens

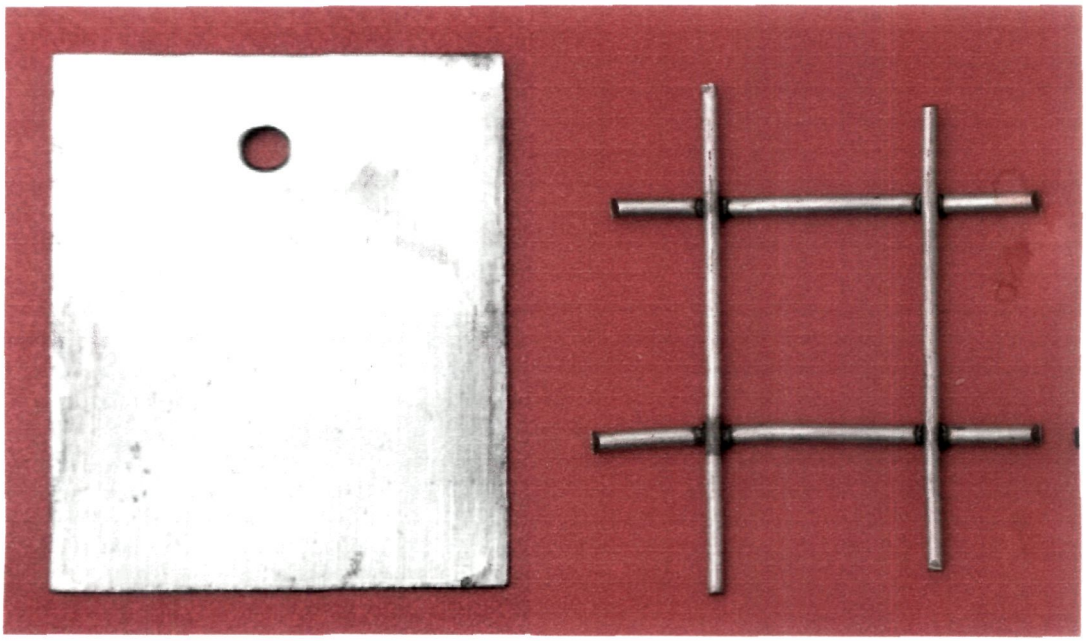


Fig. 5.4 Tannic Acid Coated Mild Steel Plate and Welded Steel Wire Mesh Specimens

5.5 COMPUTATION OF CORROSION PARAMETERS

As explained in the previous section the gravimetric weight loss study was undertaken. The loss in weight, for each exposure medium, was determined. Taking these results, corrosion parameters namely, corrosion inhibition efficiency, corrosion rate and penetration rates were calculated using the following equations (Fontana, 1987):

$$\text{Corrosion Inhibition Efficiency (\%)} = \frac{W_i - W_f}{W_i} \times 100 = \frac{W}{W_i} \times 100 \quad (5.1)$$

$$\text{Corrosion Rate } (mpy) = \frac{534 \times W}{D \times A \times T} \quad (5.2)$$

$$\text{Penetration Rate } (\mu m/year) = \text{Corrosion } Rate \ (in\ mpy) \times 25.4 \quad (5.3)$$

where,

W_i = Initial weight of the specimen in *mg*

W_f = Final weight of the specimen in *mg*

$W = W_i - W_f$ = weight loss of the specimen in *mg*

D = density of the specimen in gm/cm^3

A = surface area of the specimen in *sq. inch*

T = exposure time in *hours*

mpy = *mils per year* or *milli inch per year*

μm/year = *micro meter per year*

5.6 TESTS ON MILD STEEL PLATE SPECIMENS

After recording the initial weight, the mild steel plate specimens (Fig. 5.1), were exposed to the different mediums as per the scheme given in Table– 5.1. After the specified time of exposure, the specimens were taken out of the medium, cleaned and dried. The final weight of the specimens was then recorded. Taking the average weight loss, the corrosion inhibition efficiency, corrosion rate and penetration rate were calculated using the Eqns. 5.1 – 5.3. The results have been presented in Tables– 5.3 and 5.4 and also shown in Figs. 5.5 – 5.13. The tested mild steel plate specimens after 360 *days* of exposure under different mediums are shown in Figs. 5.14 – 5.17.

5.6.1 EFFECT OF INHIBITOR DOSE

The dose of inhibitors for the gravimetric weight loss study was chosen as one of the variable and taken as 1%, 3% and 5%. The effect of the dose of inhibitor on corrosion inhibition efficiency, corrosion rate and penetration rate has been discussed in the following sub-sections.

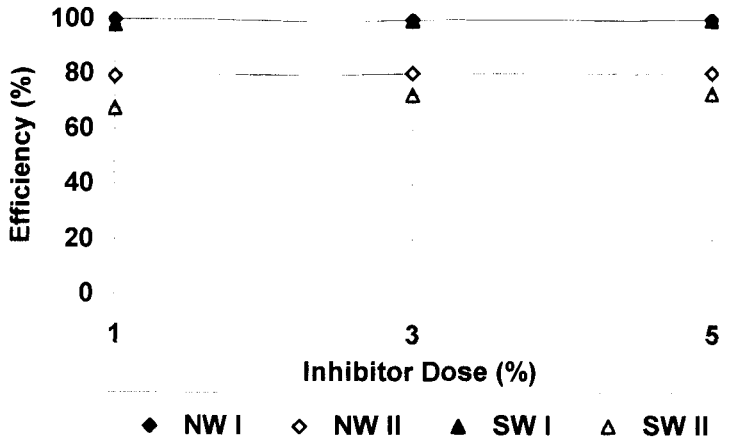
5.6.1.1 CORROSION INHIBITION EFFICIENCY

The corrosion inhibition efficiency exhibited by calcium nitrite and tannic acid for the mild steel plate specimen has been presented in Table– 5.3 and Figs. 5.5(a–d). For both the inhibitors, it has been observed that the corrosion inhibition efficiency increases with the increase in the dose of inhibitor, both in potable and saline water medium for whole duration of exposure. Extremely high efficiency has been observed for all the doses of calcium nitrite. Even at 1% dose of inhibitor, the efficiency was found to be above 97%, both in potable and saline water medium, except after 180 *days* and 360 *days* of exposure in saline water medium, where a reasonably good efficiency well above 80%, has been observed.

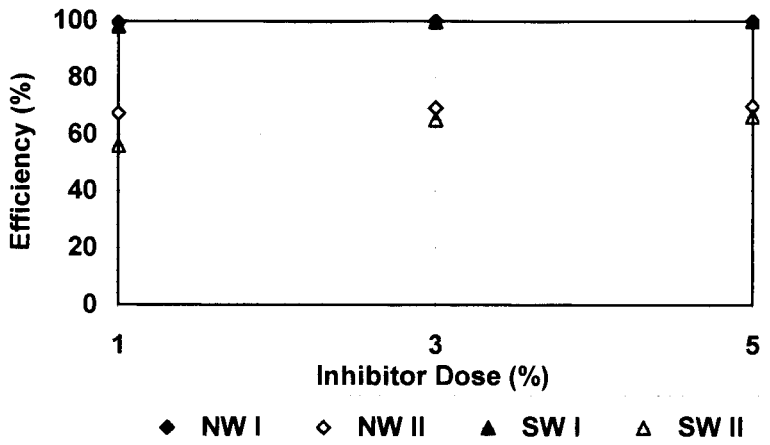
The corrosion inhibition efficiency exhibited by the tannic acid has not been found at par with calcium nitrite. In potable water medium, the efficiency was observed to be around 80% after 30 *days* of exposure which reduced to about 45% after 360 *days* of exposure, for all the doses. For the specimen inhibited with 1% tannic acid and exposed in saline water medium, the efficiency has been observed to be 67% after 30 *days* of exposure and 31% after 360 *days* of exposure. A little higher efficiency of about 72-73% after 30 *days* of exposure and 40–43% after 360 *days* of exposure has been observed for 3% and 5% dose of tannic acid. The reason behind tannic acid being not so effective in controlling corrosion is perhaps the substantial damage of the protective coating formed on metal surface, which eventually gets dissolved in aqueous solution with the passage of time.

Table– 5.3 Average Weight Loss and Corrosion Inhibition Efficiency for Mild Steel Plate

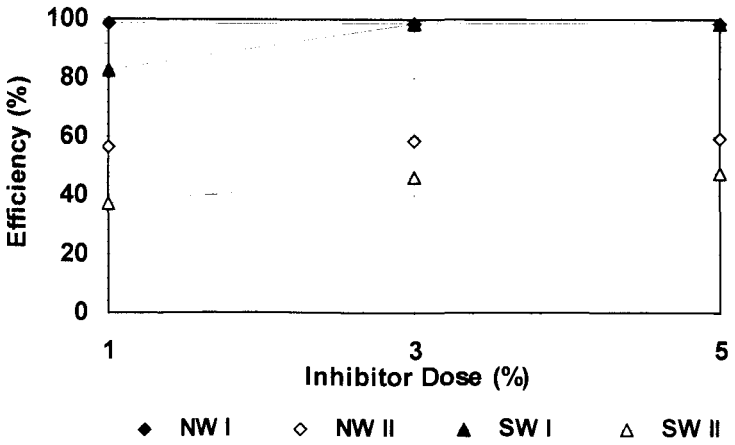
S. No.	Systems of Exposure	30 *days*		90 *days*		180 *days*		360 *days*	
		Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)
1.	NW	51.43	---	119.500	---	210.667	---	350.800	---
2.	NW I-1	0.166	99.68	0.500	99.58	2.650	98.74	8.200	97.66
3.	NW I-3	0.033	99.94	0.067	99.94	2.433	98.84	7.400	97.89
4.	NW I-5	0.000	100.00	0.000	100.00	2.400	98.86	5.100	98.55
5.	NW II-1	10.696	79.20	38.856	67.48	90.966	56.82	196.800	43.90
6.	NW II-3	10.010	80.54	36.770	69.23	87.600	58.42	190.790	45.61
7.	NW II-5	9.996	80.56	36.00	69.87	85.367	59.48	190.700	45.64
8.	SW	73.430	---	158.133	---	320.667	---	647.500	---
9.	SW I-1	1.633	97.78	2.800	98.23	54.333	83.06	123.100	80.98
10.	SW I-3	0.200	99.73	0.267	99.83	3.833	98.80	10.300	98.41
11.	SW I-5	0.100	99.86	0.167	99.89	3.567	98.89	10.000	98.45
12.	SW I-1	23.833	67.54	69.367	56.13	202.033	37.00	442.800	31.61
13.	SW II-3	20.133	72.58	55.133	65.13	173.300	45.96	388.100	40.06
14.	SW II-5	19.700	73.13	53.200	66.36	168.267	47.53	369.300	42.96



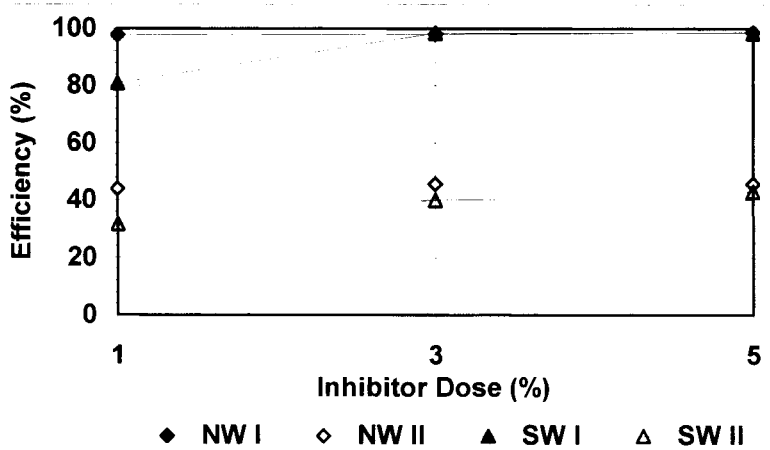
(a) 30 *days* of Exposure



(b) 90 *days* of Exposure



(c) 180 *days* of Exposure



(d) 360 *days* of Exposure

Fig. 5.5 Effect of Dose of Inhibitor on Corrosion Inhibition Efficiency for Mild Steel Plate

5.6.1.2 CORROSION RATE

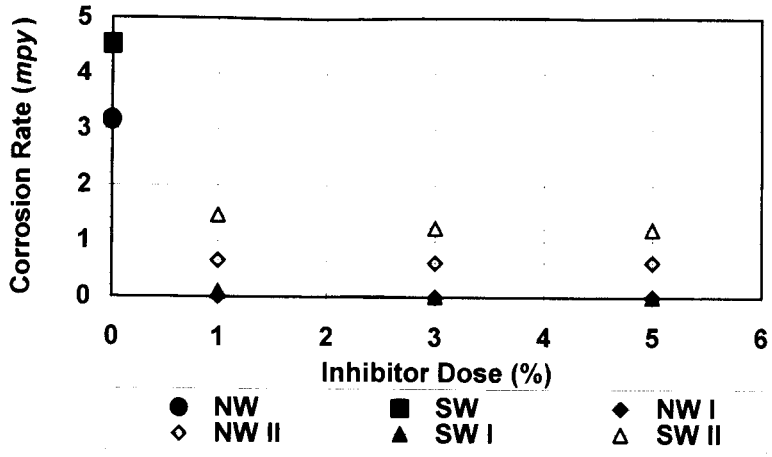
The corrosion rates exhibited by mild steel plate specimen in presence of calcium nitrite and tannic acid have been presented in Table– 5.4 and Figs. 5.6(a–d). In potable water without corrosion inhibitor (Blank- 1), the corrosion rate has been found to be lower than the corrosion rate in saline water not containing any inhibitor (Blank- 2). Calcium nitrite inhibitor exhibited extremely low corrosion rate for all the doses in potable water medium throughout the exposure duration. The specimens were observed to be almost in complete passive state even after 360 *days* of exposure. In saline water medium similar trend has been observed except for the 1% dose of calcium nitrite after 180 and 360 *days* of exposure where the corrosion rate was little higher. Tannic acid did not show as low corrosion rate as exhibited by calcium nitrite. However, the corrosion rate was observed to be lower than the corrosion rate of control specimen in respective medium of exposure for all the doses.

5.6.1.3 PENETRATION RATE

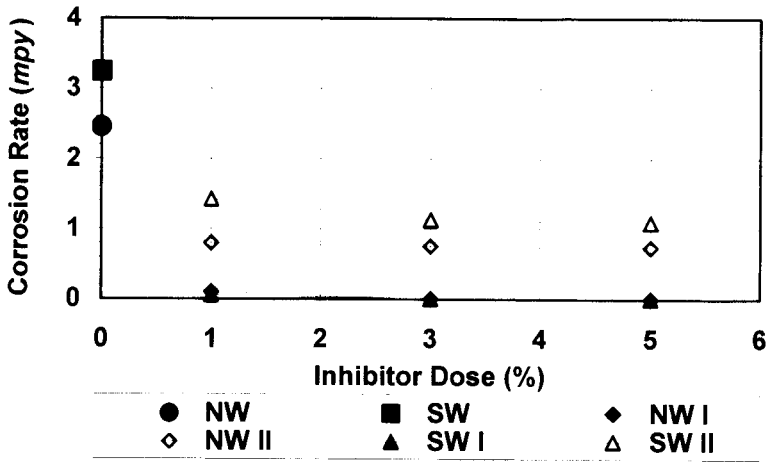
The penetration rate has been presented in Table– 5.4 and Figs. 5.7(a-d). The penetration rate has been calculated using Eqn. 5.3, which clearly shows a direct proportional relation between the corrosion rate and the penetration rate. Hence penetration rate results rightly reflect similar trend as observed in case of effect of dose of inhibitor on corrosion rate. The values of penetration rate clearly establish the effectiveness of calcium nitrite in inhibiting corrosion; however, for tannic acid the results are not so encouraging. The value of penetration rate, up to 1–2 *μm/yr* is considered to be very low to passive and the value from 2–6 *μm/yr*, is regarded as low to moderate (Law *et al.*, 2003). Based upon the results, it can be said that except for the 1% dose of calcium nitrite in saline water medium, the specimens were almost in passive state indicating the effectiveness of the calcium nitrite in controlling/delaying corrosion both in potable and saline water medium. However, for tannic acid higher values have been found which indicate very low inhibition or even negligible inhibition in some cases.

Table- 5.4 Corrosion Rate and Penetration Rate for Mild Steel Plate

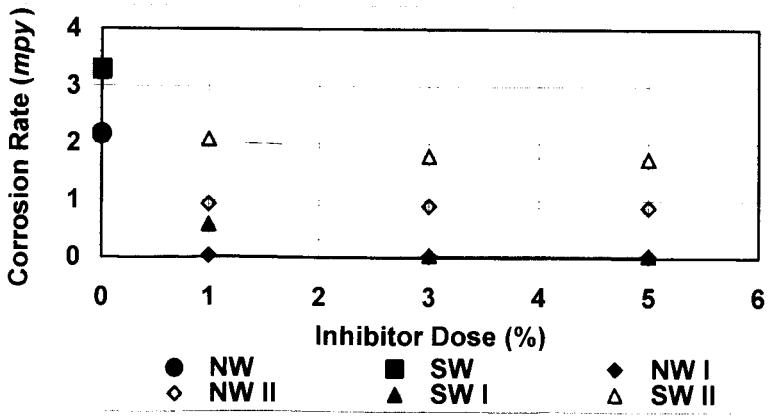
S. No.	Systems of Exposure	30 *days*		90 *days*		180 *days*		360 *days*	
		Corrosion Rate (*mpy*)	Penetration Rate (*μm/year*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/year*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/year*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/year*)
1.	NW	3.165	80.391	2.452	62.281	2.161	54.889	1.803	45.796
2.	NW I-1	0.010	0.254	0.102	2.591	0.027	0.686	0.042	1.067
3.	NW I-3	0.002	0.051	0.001	0.025	0.025	0.635	0.038	0.965
4.	NW I-5	0.000	0.000	0.000	0.000	0.025	0.635	0.026	0.660
5.	NW II-1	0.658	16.845	0.797	20.244	0.933	23.698	1.011	25.679
6.	NW II-3	0.616	15.646	0.754	19.152	0.899	22.835	0.980	24.892
7.	NW II-5	0.615	15.624	0.739	18.771	0.876	22.250	0.980	24.892
8.	SW	4.520	114.808	3.244	82.398	3.289	83.541	3.327	84.506
9.	SW I-1	0.100	2.540	0.057	1.448	0.577	14.656	0.633	16.078
10.	SW I-3	0.012	0.305	0.005	0.127	0.039	0.991	0.053	1.346
11.	SW I-5	0.006	0.152	0.003	0.076	0.037	0.940	0.051	1.295
12.	SW I-1	1.467	37.262	1.423	36.144	2.073	52.654	2.275	57.785
13.	SW II-3	1.239	37.471	1.131	28.727	1.778	45.161	1.994	50.648
14.	SW II-5	1.212	30.785	1.091	27.711	1.726	43.840	1.898	48.209



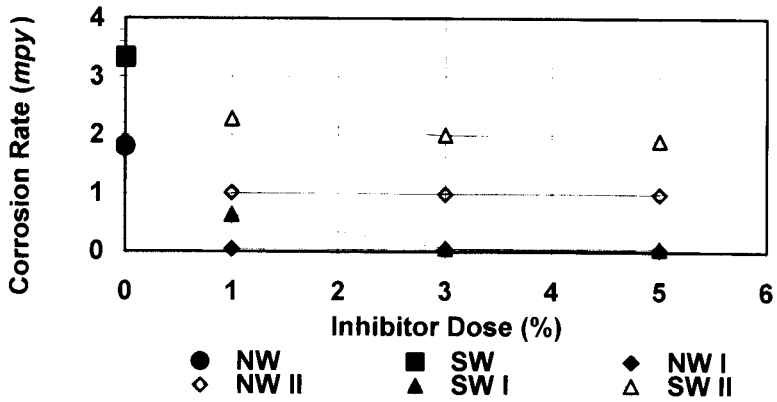
(a) 30 *days* of Exposure



(b) 90 *days* of Exposure

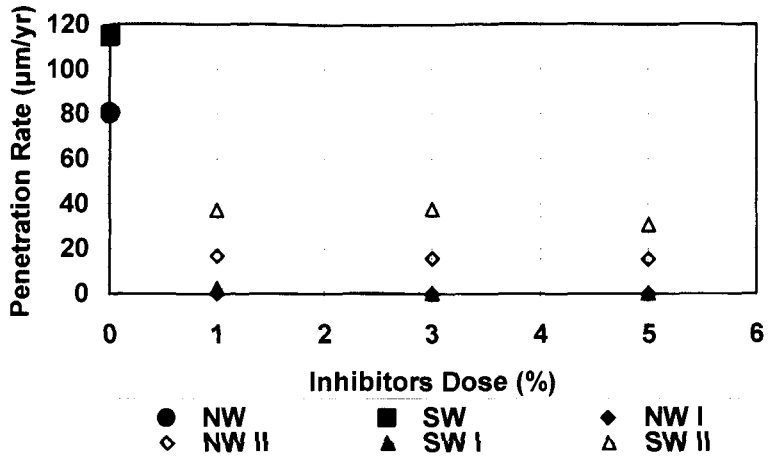


(c) 180 *days* of Exposure

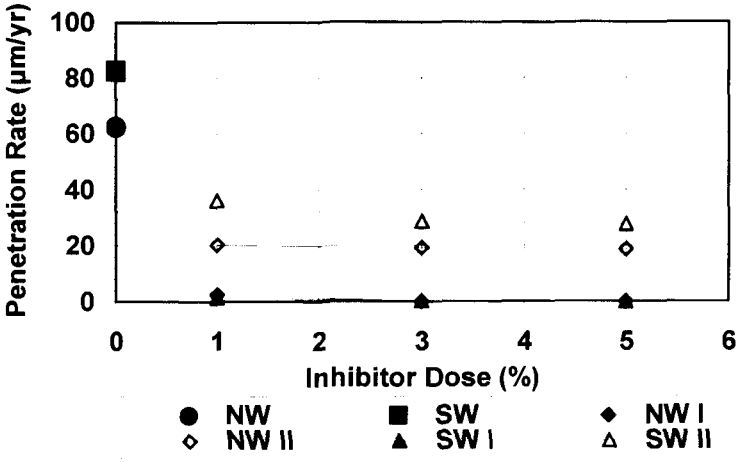


(d) 360 *days* of Exposure

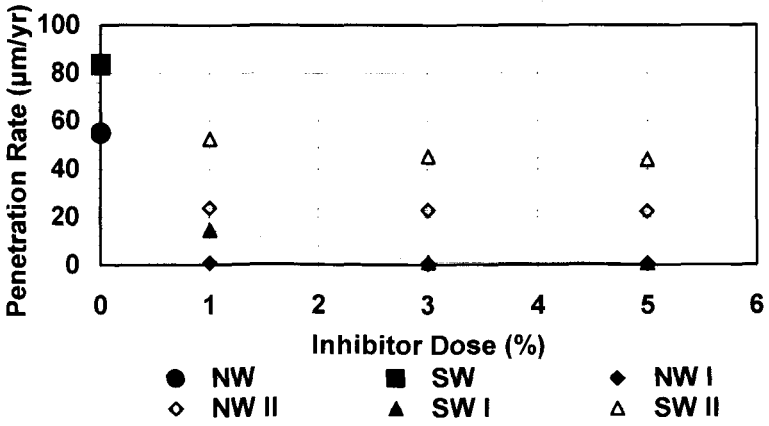
Fig. 5.6 Effect of Dose of Inhibitor on Corrosion Rate for Mild Steel Plate



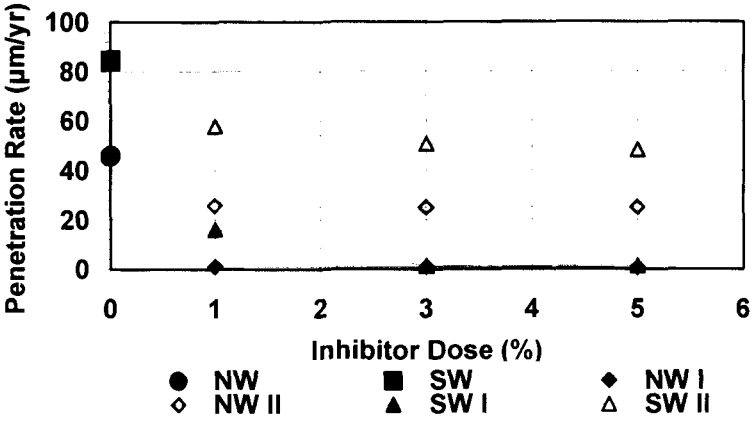
(a) 30 *days* of Exposure



(a) 90 *days* of Exposure



(a) 180 *days* of Exposure



(a) 360 *days* of Exposure

Fig. 5.7 Effect of Dose of Inhibitor on Penetration Rate for Mild Steel Plate

5.6.2 EFFECT OF EXPOSURE DURATION

In the present section the effect of the exposure duration on the corrosion inhibition efficiency, corrosion rate and the penetration rate for the mild steel plate specimen is presented. The mild steel plate specimens were exposed for 30, 90, 180 and 360 *days*. The effect of the exposure duration on corrosion inhibition efficiency, corrosion rate and penetration rate has been presented in the following sub-sections.

5.6.2.1 CORROSION INHIBITION EFFICIENCY

For calcium nitrite and tannic acid, the effect of exposure duration on the corrosion inhibition efficiency has been presented in Table– 5.3 and Figs. 5.8 – 5.9. In potable water medium excellent corrosion inhibition efficiency is exhibited by the calcium nitrite which remains almost constant with the passage of time. However, for the tannic acid the corrosion inhibition efficiency reduces sharply for longer duration of exposure. In saline water medium, similar trend is exhibited by the calcium nitrite, except for 1% inhibitor dose where the efficiency reduces after 180 and 360 *days* of exposure. For the tannic acid in the saline water medium, almost similar trend as seen in potable water medium is observed.

5.6.2.2 CORROSION RATE

The effect of exposure duration on corrosion rate for calcium nitrite and tannic acid has been presented in Table– 5.4 and Figs. 5.10 – 5.11. A lower corrosion rate has been observed for the inhibited medium in both the potable and saline water as compared to the corresponding blank specimens. This observation holds at all the four stages of exposure duration *viz.* 30, 90, 180 and 360 *days*. The observations clearly establish the effectiveness of the corrosion inhibitors in controlling/delaying the corrosion process. However, the amount of inhibition has not been the same for all the specimen groups for both the inhibitors. It is observed from Figs. 5.10 and 5.11, that the specimen exposed in calcium nitrite inhibited solution, exhibits almost negligible corrosion rate, indicating almost passive state throughout the full exposure duration. For the tannic acid inhibited specimen, the corrosion rate is found to increase with the increase in exposure duration. However, the rate of change in corrosion rate reduces as the exposure duration is increased.

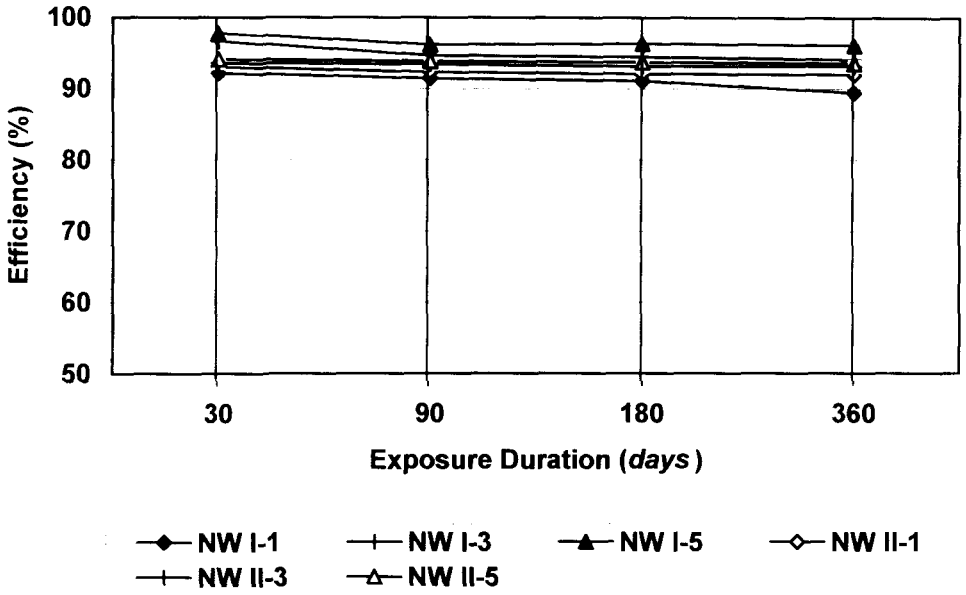


Fig. 5.8 Efficiency of Corrosion Inhibitors for Mild Steel Plate in Potable Water Medium

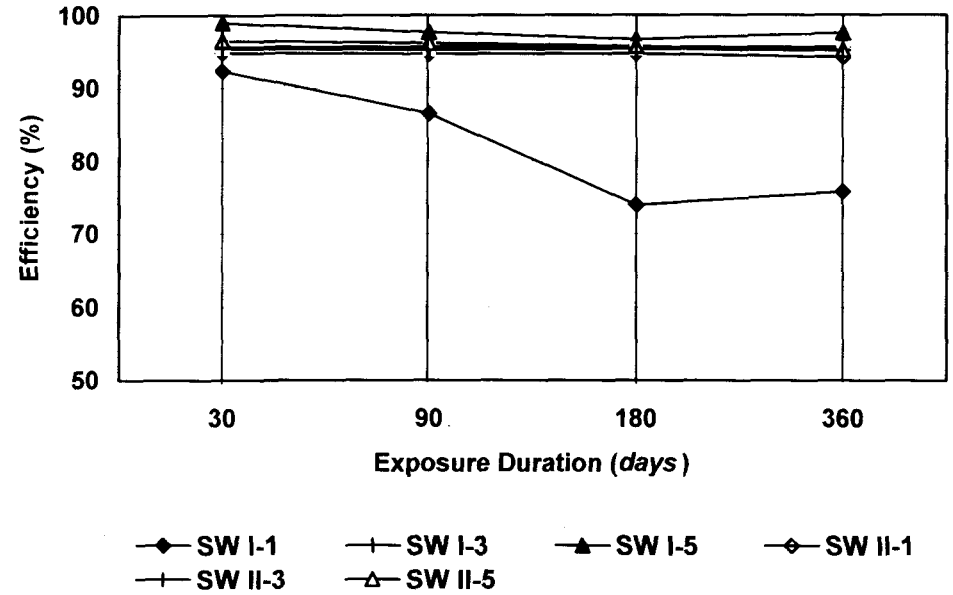


Fig. 5.9 Efficiency of Corrosion Inhibitors for Mild Steel Plate in Saline Water Medium

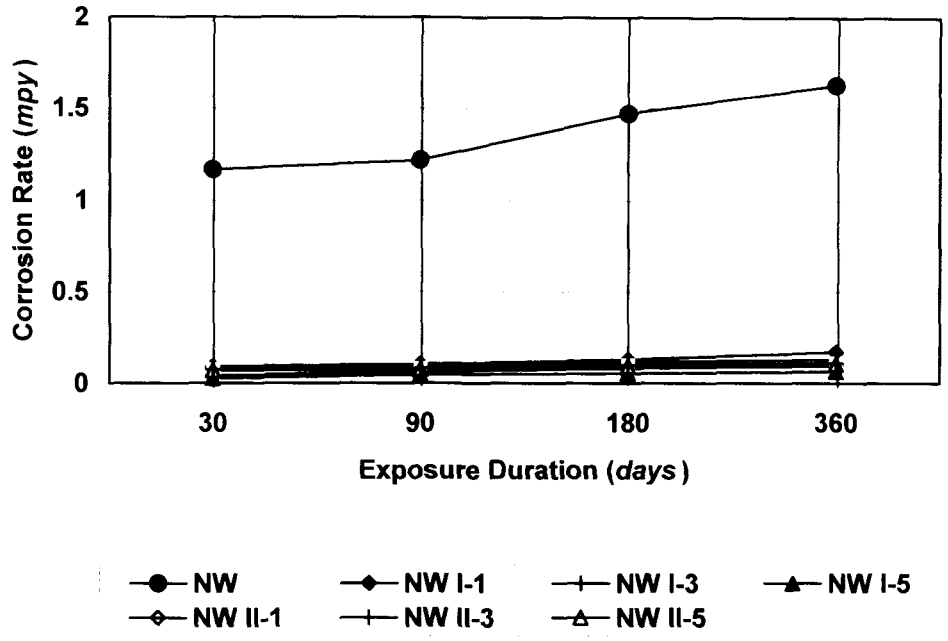


Fig. 5.10 Corrosion Rate for Mild Steel Plate in Potable Water Medium

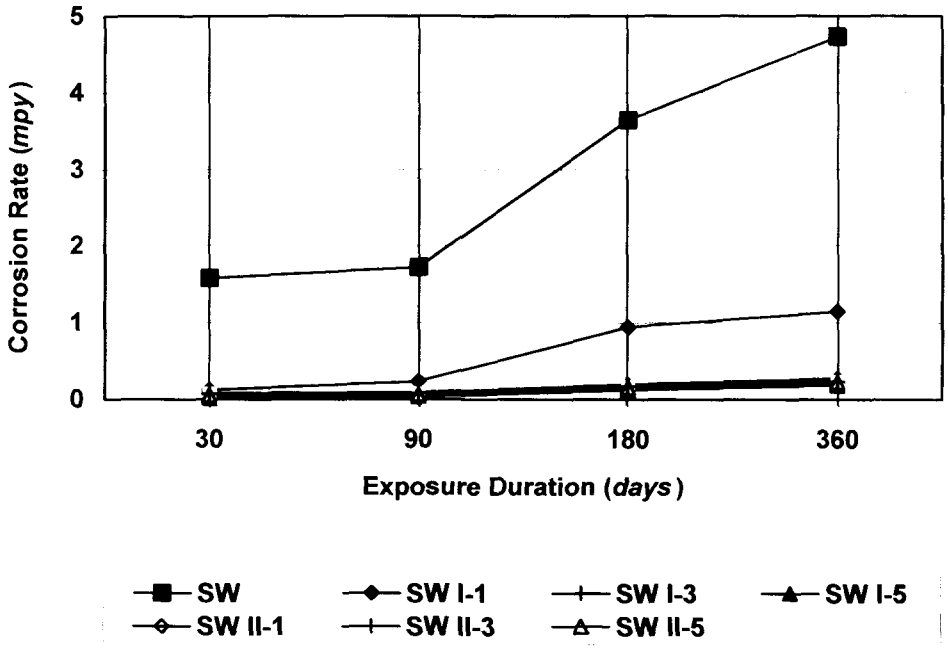


Fig. 5.11 Corrosion Rate for Mild Steel Plate in Saline Water Medium

5.6.2.3 PENETRATION RATE

The effect of exposure duration on the penetration rate has been presented in Table– 5.4 and Figs. 5.12 – 5.13. A trend similar to that of corrosion rate has been observed in case of penetration rate also. The penetration rate remains well within the acceptable limit for calcium nitrite inhibited medium for whole of the exposure duration. Although for tannic acid inhibited medium, the penetration rate values are quite high; still these are less than the values for the un-inhibited blank medium.

5.6.3 VISUAL INSPECTION

In Figs. 5.14 – 5.17 some of the specimens after 360 *days* of exposure have been shown. Each photograph contains one blank specimen and three inhibited specimens with a particular type and the dose of inhibitors. It has been observed that the specimens exposed in calcium nitrite inhibited potable water medium have no signs of corrosion on both the faces even at 1% dose. No trace of corrosion has also been noticed in calcium nitrite inhibited saline water medium for 3% and 5% dose of inhibitor. However, for 1% dose of calcium nitrite inhibitor in saline water medium, mild surface corrosion is observed to occur over about 75% of the surface area. For specimen inhibited with tannic acid and exposed in potable water medium, full surface area undergoes mild to moderate corrosion, however, in saline water medium severe corrosion is seen over the full surface of the specimen. The visual observations therefore, validate the results presented in the previous sections.

5.6.4 MICROSCOPIC EXAMINATION

For undertaking the microscopic examination of mild steel plate specimens, a high magnification microscope was used. The investigations were carried out in the High Resolution Microscope Lab. of the Applied Physics Department, Z.H. College of Engineering and Technology, A.M.U., Aligarh (India). The images of the mild steel plate specimens were captured at a magnification of 400X. Figures 5.18 – 5.19 represent images of mild steel plate specimens along with the control and inhibited specimens after 360 *days* of exposure in different exposure mediums.

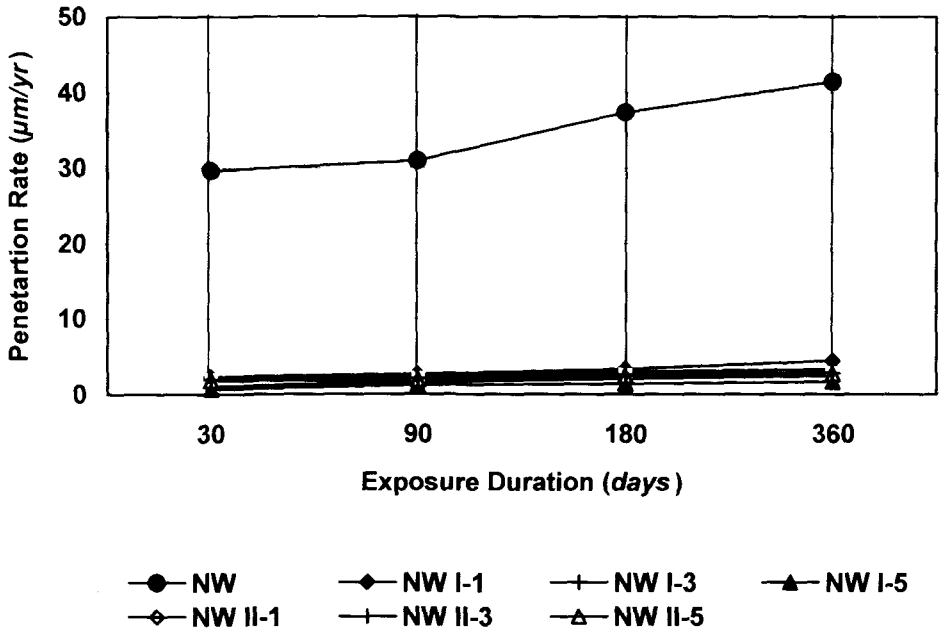


Fig. 5.12 Penetration Rate for Mild Steel Plate in Potable Water Medium

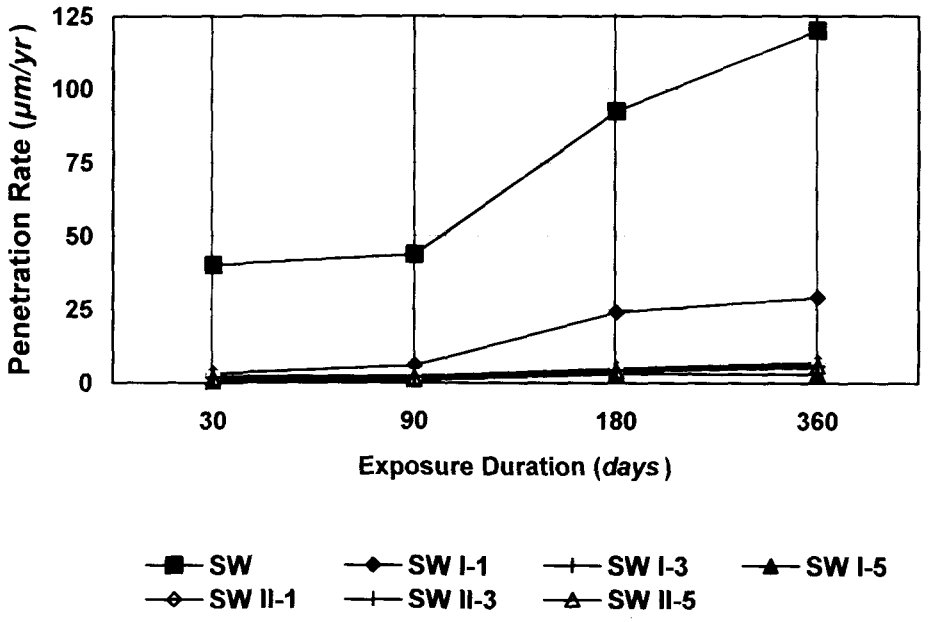


Fig. 5.13 Penetration Rate for Mild Steel Plate in Saline Water Medium

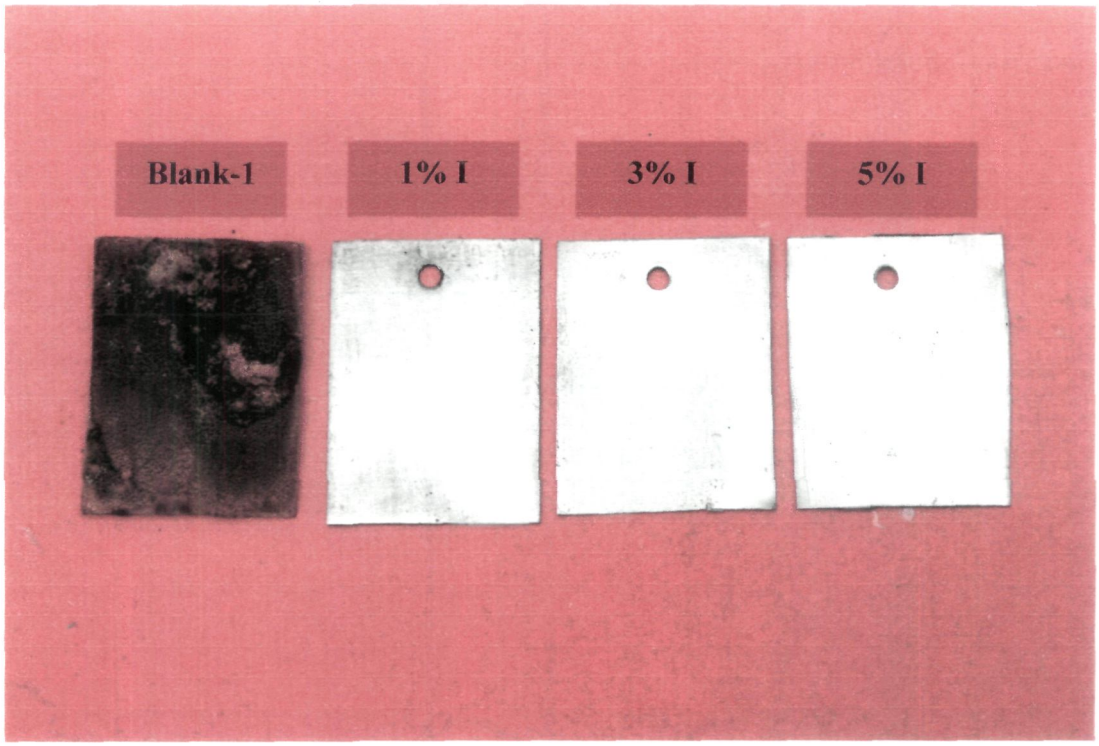


Fig. 5.14 **Mild Steel Plate Specimen after 360 *days* of Exposure in Potable Water Medium (Blank and Calcium Nitrite Inhibited)**

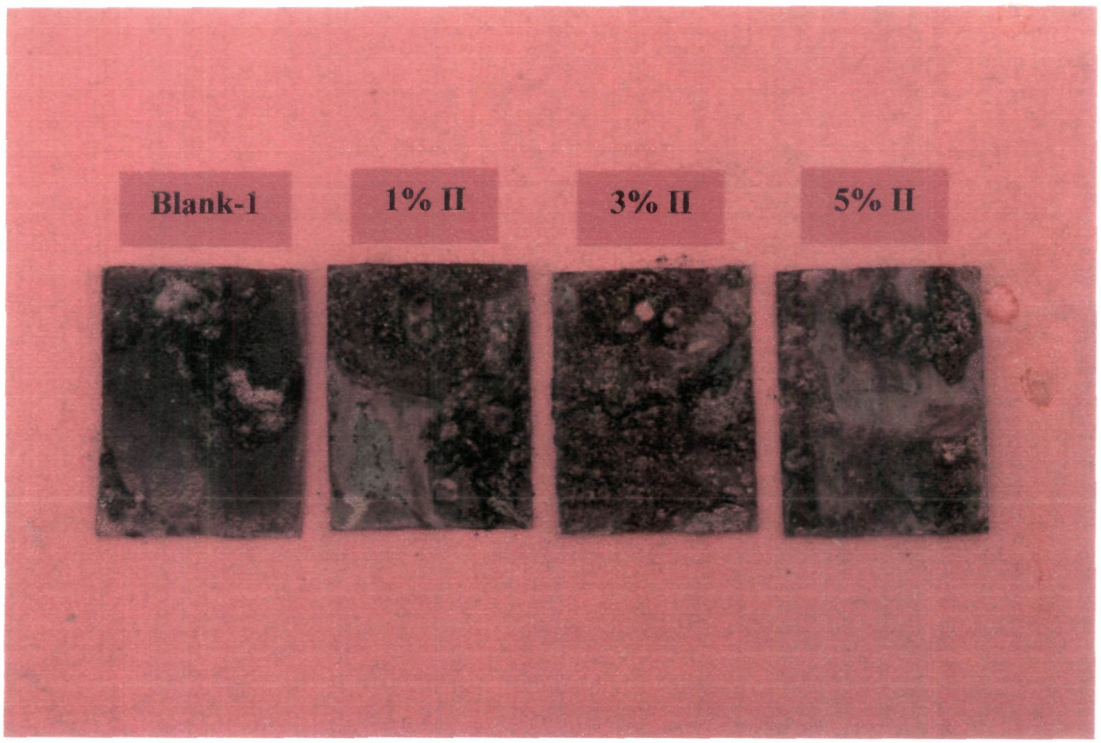


Fig. 5.15 **Mild Steel Plate Specimen after 360 *days* of Exposure in Potable Water Medium (Blank and Tannic Acid Inhibited)**

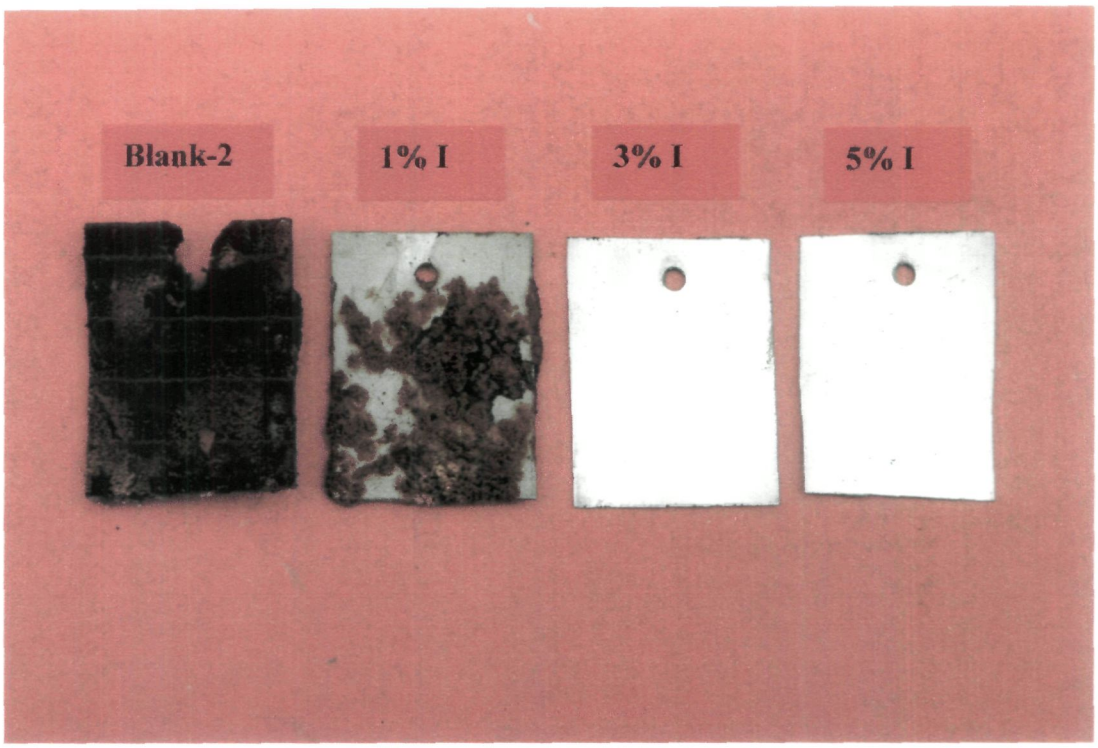


Fig. 5.16 **Mild Steel Plate Specimen after 360 *days* of Exposure in Saline Water Medium (Blank and Calcium Nitrite Inhibited)**

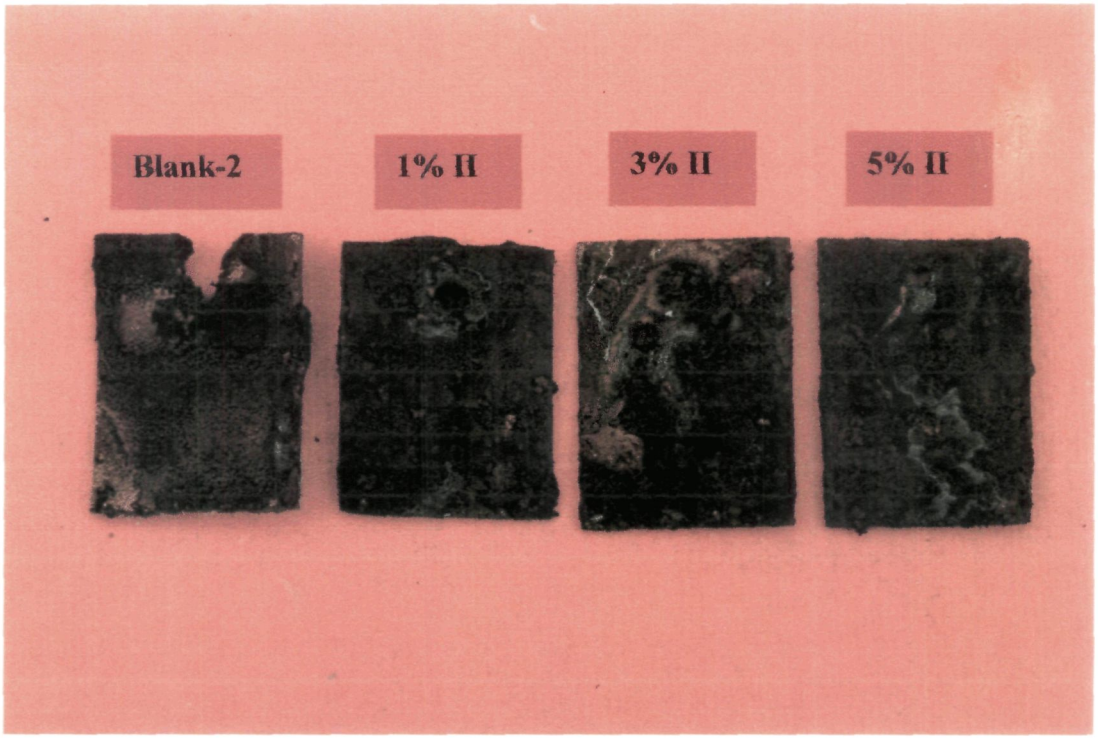
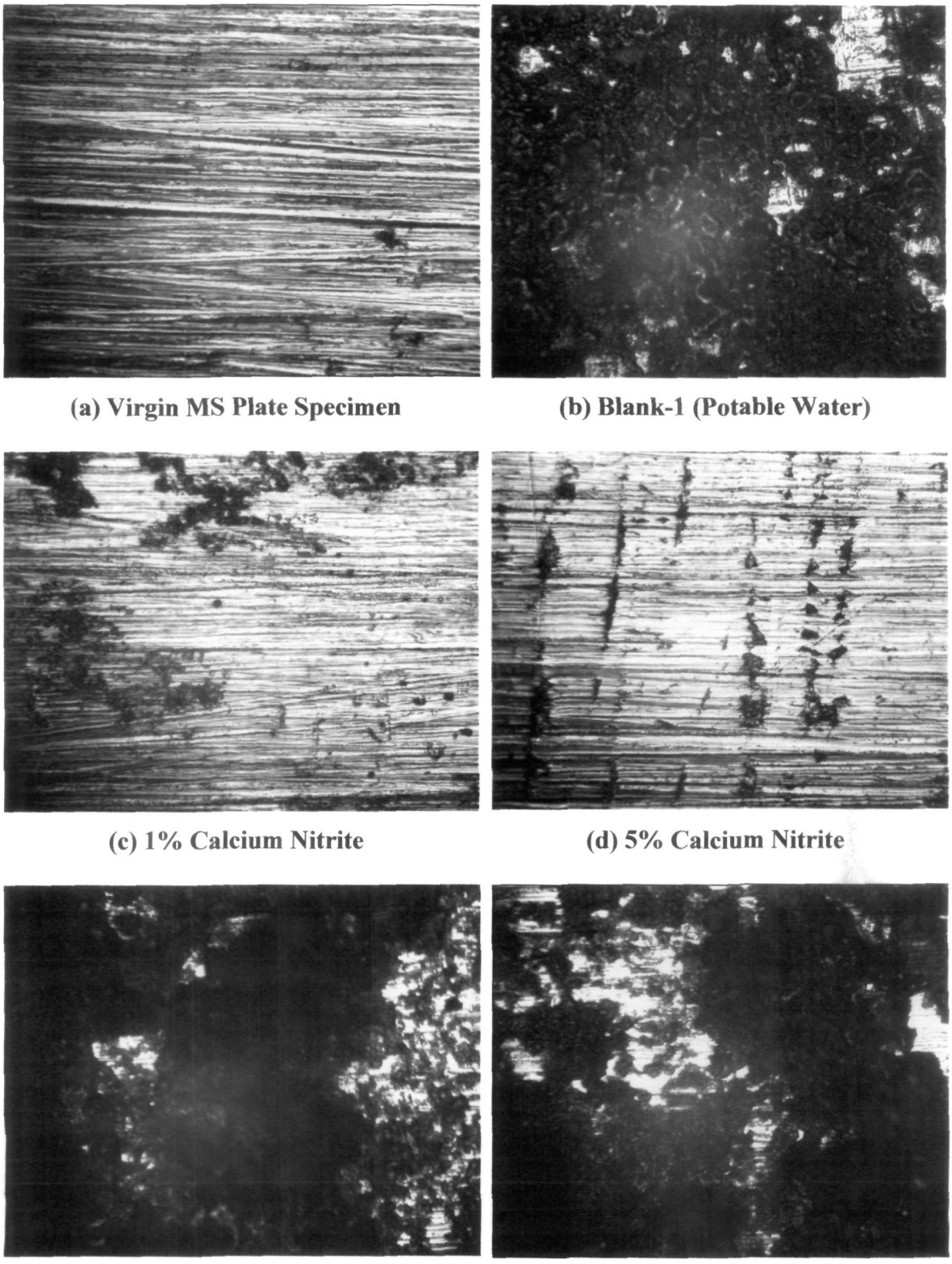


Fig. 5.17 **Mild Steel Plate Specimen after 360 *days* of Exposure in Saline Water Medium (Blank and Tannic Acid Inhibited)**



(a) Virgin MS Plate Specimen

(b) Blank-1 (Potable Water)

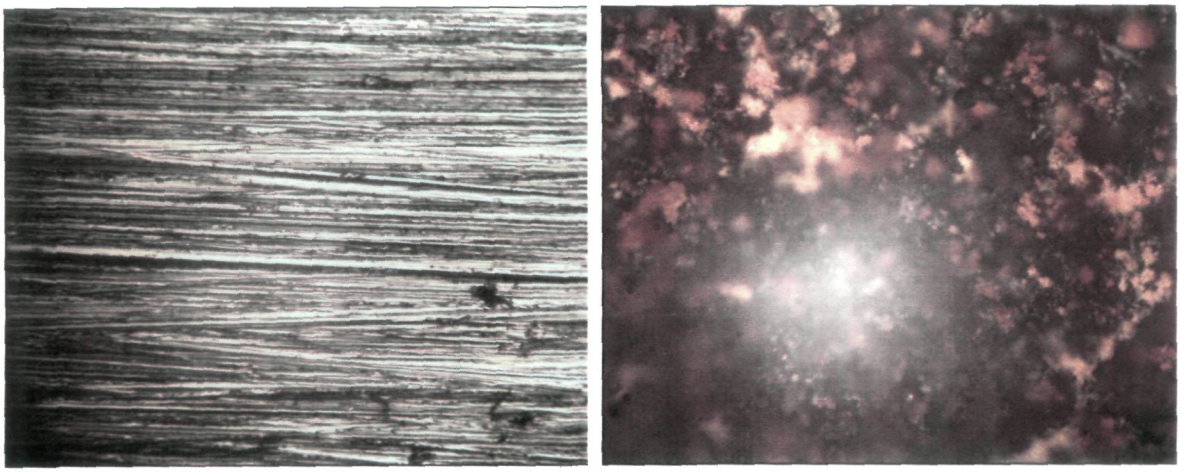
(c) 1% Calcium Nitrite

(d) 5% Calcium Nitrite

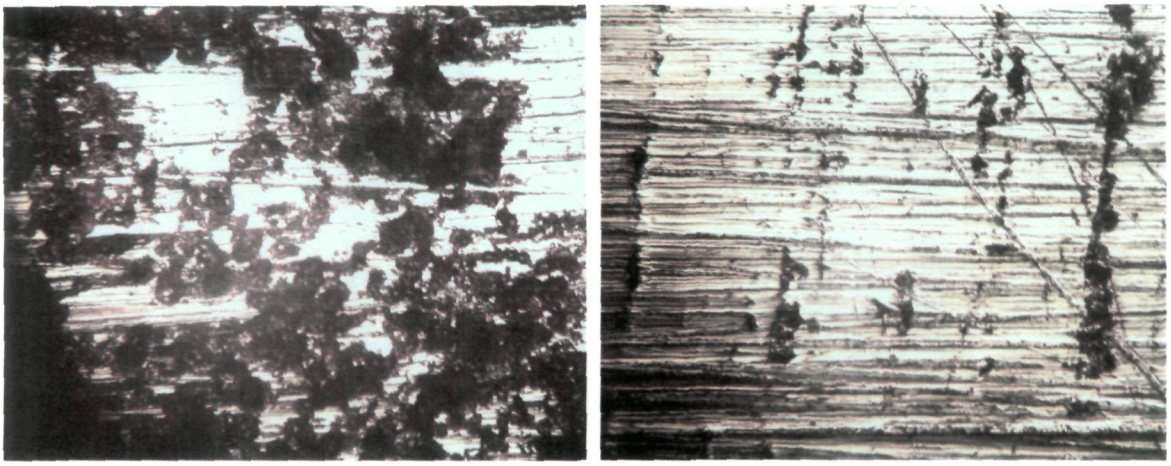
(e) 1% Tannic Acid

(f) 5% Tannic Acid

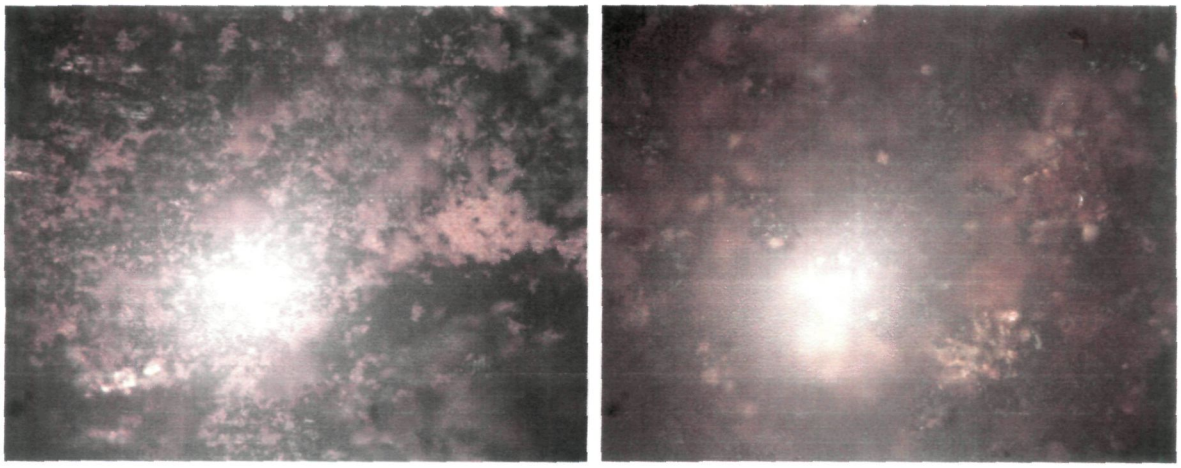
Fig. 5.18 Microscopic Images at 400X Magnification of MS Plate Specimen after 360 *days* of Exposure in Potable Water Medium



(a) Virgin MS Plate Specimen (b) Blank-2 (Saline Water)



(c) 1% Calcium Nitrite (d) 5% Calcium Nitrite



(e) 1% Tannic Acid (f) 5% Tannic Acid

Fig. 5.19 Microscopic Images at 400X Magnification of MS Plate Specimen after 360 *days* of Exposure in Saline Water Medium

A quick glance at these images makes it explicitly clear that the corrosion inhibitors play a key role in mitigating/controlling corrosion in the mild steel plate in both potable and saline water exposure medium.

In the Figs. 5.18(a) and 5.19(a), the magnified image of virgin mild steel plate has been shown which clearly displays the corrosion free and spotless virgin surface of the specimen. The mild steel plate specimen exposed in blank potable water medium after 360 *days* of exposure duration has been shown in Fig. 5.18(b) where the ingress of corrosion, spread over almost entire plate specimen surface, can be witnessed. The plate specimen inhibited with 1% calcium nitrite has been shown in Fig. 5.18(c) where little corrosion activity can be viewed. In the Fig. 5.18(d), the mild steel plate specimens with 5% calcium nitrite has been shown wherein almost rare to very little corrosion activity has been noticed thus clearly establishing the effectiveness of corrosion inhibitor in mitigating corrosion.

Another important information gathered here is about the tannic acid not been so effective in controlling corrosion at 1% dose and also at a dose of 5%, as may be seen in Figs. 5.18(e) and 5.18(f), where the corrosion activity continues to be unabated rendering the entire surface manifested with corrosion action. The entire plate surface undergoes mild to moderate corrosion.

The mild steel plate specimen exposed in blank saline water medium after 360 *days* of exposure duration has been shown in Fig. 5.19(b), where the most severe ingress of corrosion spread over entire plate specimen surface is clearly visible. The plate specimen inhibited with 1% calcium nitrite has been shown in Fig. 5.19(c) where sporadic traces of corrosion activity can be viewed covering about 75% of the plate surface area indicating a medium to mild surface corrosion. In the Fig. 5.19(d), the mild steel plate specimens with 5% calcium nitrite has been shown wherein mild to very little corrosion activity has been noticed which clearly establishes the worthiness of corrosion inhibitor in mitigating corrosion. However, tannic acid has not been so effective in controlling corrosion both at 1% dose and with no significant change even at a dose of 5%, as may be seen in Figs. 5.19(e) and 5.19(f), where the corrosion activity continues to be unabated rendering the entire surface manifested with corrosion action.

The comparison of the images of the inhibited specimen with the virgin and control specimen makes it clear that calcium nitrite is able to inhibit corrosion even at 1% concentration in potable water; however a mild corrosion has been observed at this concentration in saline water medium. At higher dose, very high inhibition is observed both in saline and potable water medium. Tannic acid however, has not been found to be effective in mitigating corrosion. These observations move in line with the gravimetric weight loss results and visual inspection of the specimens as explained in the previous sections.

5.7 TESTS ON NAKED WELDED STEEL WIRE MESH SPECIMENS

After recording their initial weight, the naked welded steel wire mesh specimens as shown in Fig. 5.2 were exposed to the different mediums as per the scheme given in Table– 5.1. After the specified time of exposure, the specimens were taken out of the medium, cleaned and dried. The final weight of the specimens was then recorded. The corrosion inhibition efficiency, corrosion rate and penetration rate were calculated using the observed weight loss as per Eqns. 5.1 – 5.3. The results have been presented in Tables– 5.5 and 5.6 and shown in Figs. 5.20 – 5.28. The tested naked welded steel wire mesh specimens after 360 *days* of exposure under different mediums are shown in Figs. 5.29 – 5.32.

5.7.1 EFFECT OF INHIBITOR DOSE

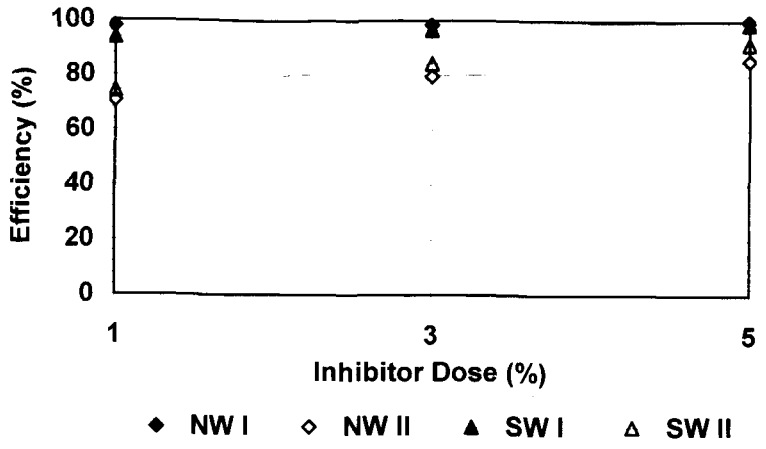
The dose of the inhibitors was varied as 1%, 3% and 5% for both calcium nitrite and tannic acid. The effect of the variation of the dose of corrosion inhibitors on corrosion inhibition efficiency, corrosion rate and penetration rate has been discussed in the following sub-sections.

5.7.1.1 CORROSION INHIBITION EFFICIENCY

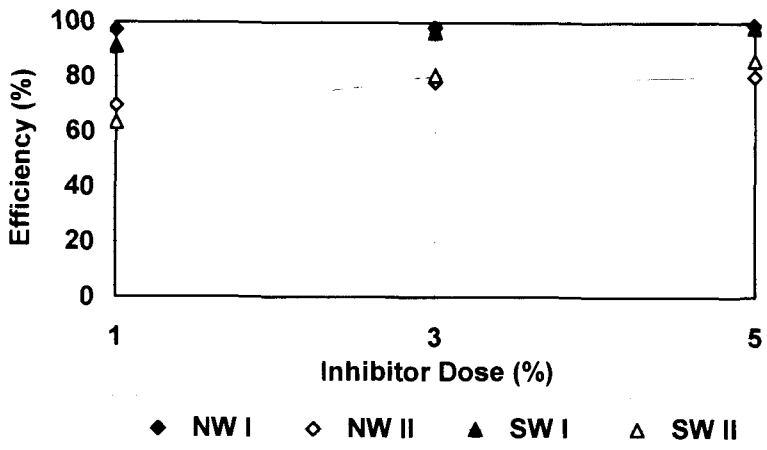
For the naked welded steel wire mesh specimens, corrosion inhibition efficiency exhibited by calcium nitrite and tannic acid has been presented in Table– 5.5 and Figs. 5.20(a-d). For both potable as well as saline water medium, the corrosion inhibition efficiency increases with the increase in the dose of inhibitor.

Table– 5.5 Average Weight Loss and Corrosion Inhibition Efficiency for Naked Welded Steel Wire Mesh

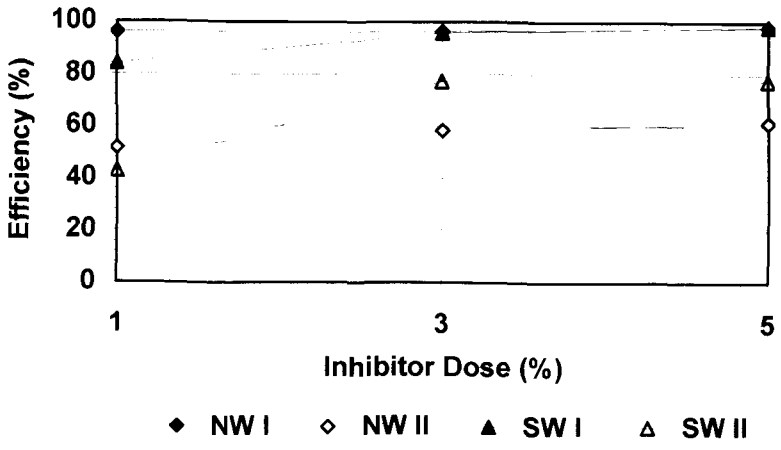
S. No.	Systems of Exposure	30 *days*		90 *days*		180 *days*		360 *days*	
		Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)
1.	NW	11.900	---	37.300	---	90.200	---	200.00	---
2.	NW I-1	0.267	97.77	1.033	97.23	3.500	96.12	7.100	96.45
3.	NW I-3	0.200	98.32	0.700	98.12	2.967	96.17	6.000	97.00
4.	NW I-5	0.033	99.72	0.367	99.02	1.833	97.97	4.200	97.90
5.	NW II-1	3.500	70.59	11.333	69.62	43.733	51.51	153.667	23.16
6.	NW II-3	2.433	79.55	8.100	78.28	37.667	58.24	114.700	42.65
7.	NW II-5	1.733	85.44	6.330	80.35	35.000	61.20	109.300	45.35
8.	SW	16.133	---	52.667	---	223.000	---	579.300	---
9.	SW I-1	1.067	93.93	4.600	91.26	45.467	84.10	94.330	83.72
10.	SW I-3	0.567	96.48	1.833	96.52	9.667	95.67	26.000	95.51
11.	SW I-5	0.200	98.76	0.933	98.22	3.967	98.22	8.200	98.58
12.	SW I-1	4.133	74.38	19.200	63.54	127.064	43.02	478.833	17.34
13.	SW II-3	2.533	84.30	10.133	80.76	51.100	77.10	139.033	76.00
14.	SW II-5	1.933	91.53	7.367	86.01	50.167	77.50	138.033	76.17



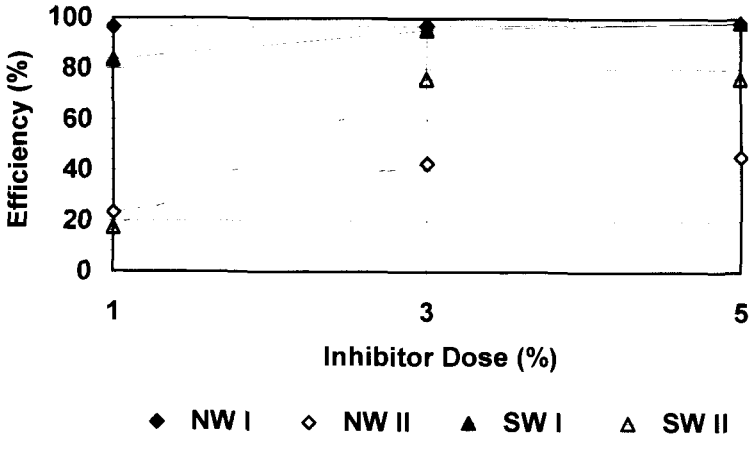
(a) 30 *days* of Exposure



(b) 90 *days* of Exposure



(c) 180 *days* of Exposure



(d) 360 *days* of Exposure

Fig. 5.20 Effect of Dose of Inhibitor on Corrosion Inhibition Efficiency for Naked Welded Steel Wire Mesh

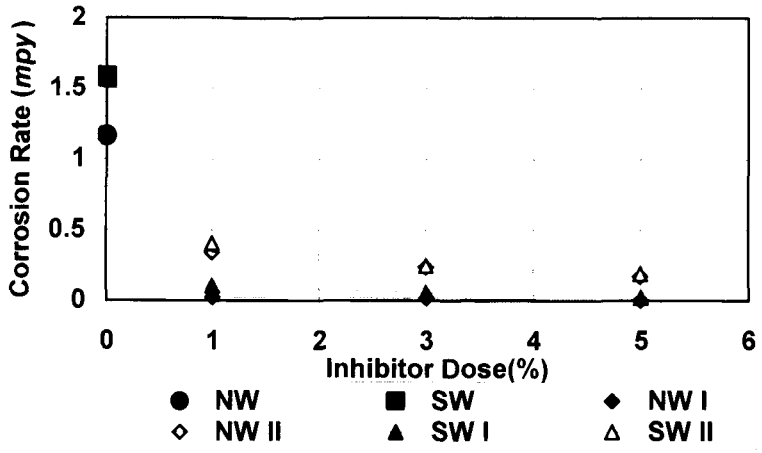
This observation holds for all the exposure durations, for both of the inhibitors. For all the doses of calcium nitrite in potable water medium, extremely high efficiency well above 96% has been observed. In saline water medium, the corrosion inhibition efficiency is observed to be above as 95% for 3% and 5% inhibitor dose. Even at 1% dose of calcium nitrite, the efficiency was found to be above 90% after 30 and 90 *days* of exposure. For 180 and 360 *days* of exposure duration, the efficiency reduces to around 80%, nevertheless, continues to be quite satisfactory and well acceptable. The level of corrosion inhibition efficiency exhibited by the tannic acid was reasonably high at initial stages of exposure for all the doses, however, low efficiency at lower doses is observed for longer duration of exposure. In potable water medium, the efficiency was found to be 70%, 79% and 85% after 30 *days* of exposure and down to 23%, 42% and 45% after 360 *days* of exposure, respectively for 1%, 3% and 5% dose of tannic acid. For the saline water medium, efficiency has been observed to be 74%, 84% and 91% after 30 *days* of exposure and down to 17%, 76% and 76% after 360 *days* of exposure, respectively for 1%, 3% and 5% dose. The reason behind tannic acid not been so effective in controlling corrosion, is the same as observed for mild steel plate specimen, *i.e.* the protective coating formed on metal surface perhaps dissolves in aqueous solution with the passage of time thereby, rendering the specimen vulnerable to the hostile surroundings.

5.7.1.2 CORROSION RATE

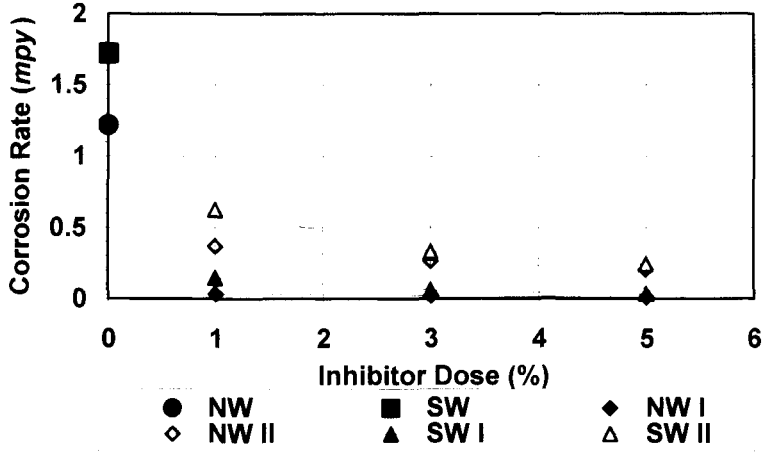
For the naked welded steel wire mesh specimens, the corrosion rate has been presented in Table– 5.6 and Figs. 5.21(a-d). In potable water medium without corrosion inhibitor (Blank-1), the corrosion rate has been found to be lower than the corrosion rate in saline water medium without corrosion inhibitor (Blank-2). Calcium nitrite inhibitor exhibited extremely low corrosion rate for all the doses in potable water medium throughout the exposure duration. The specimens were observed to be almost in complete passive state even after 360 *days* of exposure. In saline water medium, similar trend has been observed except for the 1% dose of calcium nitrite after 180 and 360 *days* of exposure, where the corrosion rate was little higher. Tannic acid did not show that low corrosion rate as exhibited by calcium nitrite. At 1% dose of tannic acid, quite significant rate of corrosion is observed.

Table– 5.6 Corrosion Rate and Penetration rate for Naked Welded Steel Wire Mesh

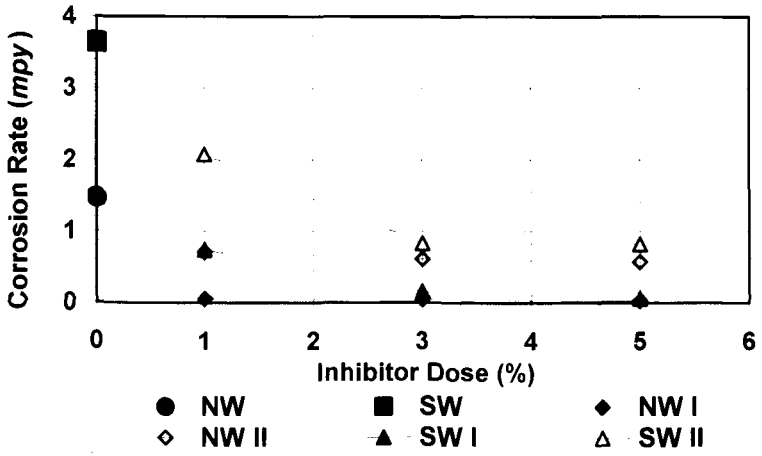
S. No.	Systems of Exposure	30 *days*		90 *days*		180 *days*		360 *days*	
		Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)
1.	NW	1.166	29.616	1.219	30.963	1.473	37.414	1.633	41.478
2.	NW I-1	0.026	0.660	0.034	0.864	0.057	1.448	0.058	1.473
3.	NW I-3	0.020	0.508	0.023	0.584	0.048	1.219	0.049	1.245
4.	NW I-5	0.003	0.076	0.012	0.305	0.030	0.762	0.034	0.864
5.	NW II-1	0.343	8.712	0.370	9.398	0.714	18.136	1.255	31.877
6.	NW II-3	0.238	6.045	0.265	6.731	0.615	15.621	0.937	23.800
7.	NW II-5	0.170	4.318	0.207	3.142	0.573	14.554	0.893	22.682
8.	SW	1.581	40.132	1.721	43.713	3.643	92.530	4.731	120.167
9.	SW I-1	0.105	2.667	0.150	3.142	0.743	18.870	0.770	19.558
10.	SW I-3	0.056	1.422	0.060	1.524	0.158	4.013	0.212	5.385
11.	SW I-5	0.020	0.508	0.033	0.838	0.065	1.651	0.067	1.702
12.	SW I-1	0.405	10.287	0.627	15.926	2.076	52.730	3.911	99.339
13.	SW II-3	0.248	6.299	0.331	8.407	0.835	21.209	1.135	28.829
14.	SW II-5	0.189	4.801	0.241	6.121	0.819	20.803	1.127	28.626



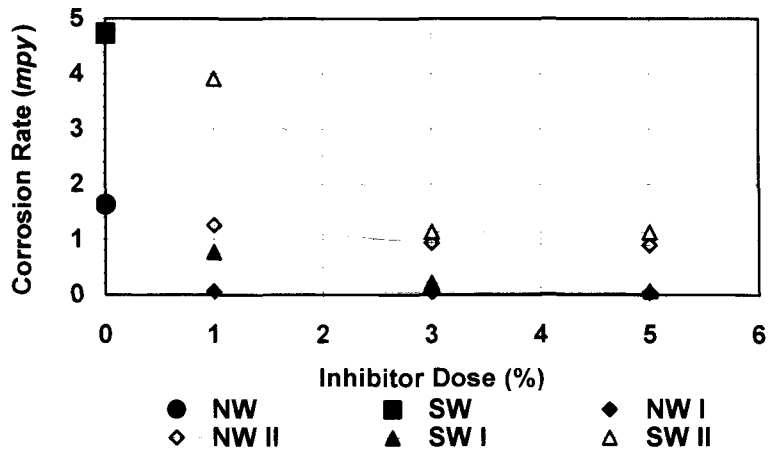
(a) 30 *days* of Exposure



(a) 90 *days* of Exposure



(a) 180 *days* of Exposure



(a) 360 *days* of Exposure

Fig. 5.21 Effect of Dose of Inhibitor on Corrosion Rate for Naked Welded Steel Wire Mesh

As the inhibitor dose is increased to 3%, the corrosion rate reduces sharply, and remains unchanged even at 5% dose of tannic acid. In general, the value of corrosion rate for the inhibited environment was observed to be lower than the corrosion rate of control specimen, indicating the effectiveness of the corrosion inhibitors.

5.7.1.3 PENETRATION RATE

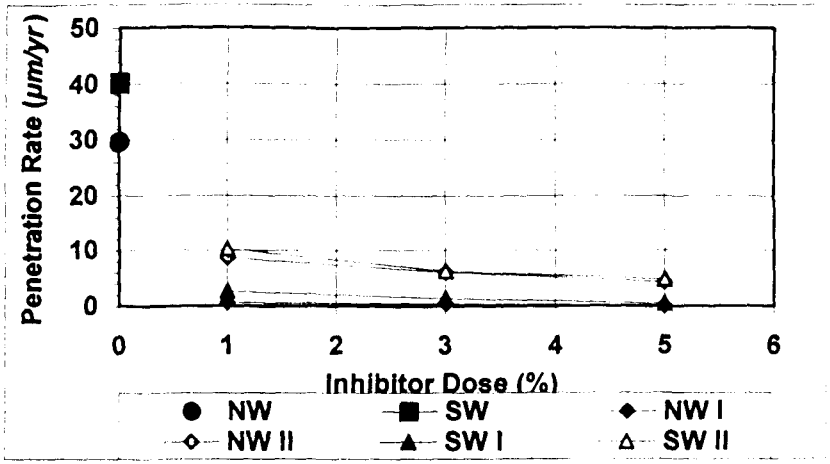
The penetration rate has been presented in Table– 5.6 and Figs. 5.22(a-d). The values of penetration rate impart extremely satisfactory results for calcium nitrite in potable water medium (< 2 *μm/yr*). However, in saline water medium at 1% dose for all exposure duration and at 3% dose of calcium nitrite for 180 *days* and 360 *days* of exposure duration the penetration rate was found to be between 2–6 *μm/yr*, which is also quite satisfactory and acceptable. At 5% dose of calcium nitrite in saline water medium, penetration rate almost similar to that of potable water has been obtained, indicating a complete passive state. For tannic acid, higher values of penetration rate are found indicating very low inhibition or negligible inhibition that too even at early stages of exposure.

5.7.2 EFFECT OF EXPOSURE DURATION

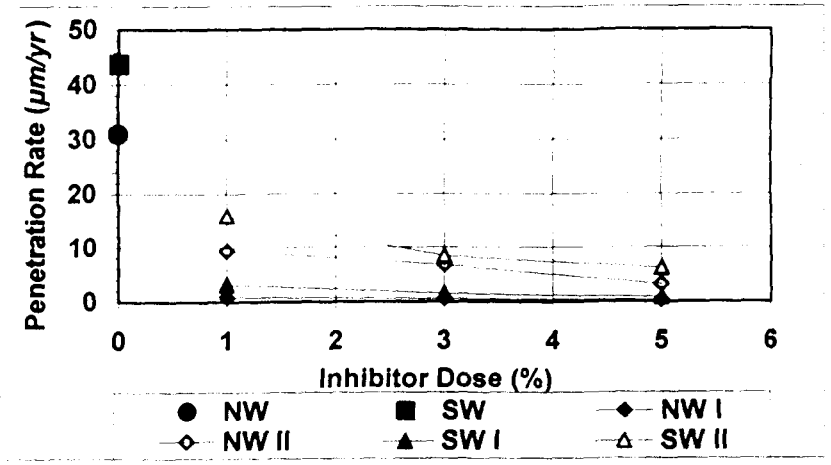
The effect of the exposure duration on the corrosion inhibition efficiency, corrosion rate and the penetration rate for the naked welded steel wire mesh specimen is discussed in this section. The naked welded steel wire mesh specimens were exposed for 30, 90, 180 and 360 *days*. The effect of the exposure duration on corrosion inhibition efficiency, corrosion rate and penetration rate has been presented in the following sub-sections.

5.7.2.1 CORROSION INHIBITION EFFICIENCY

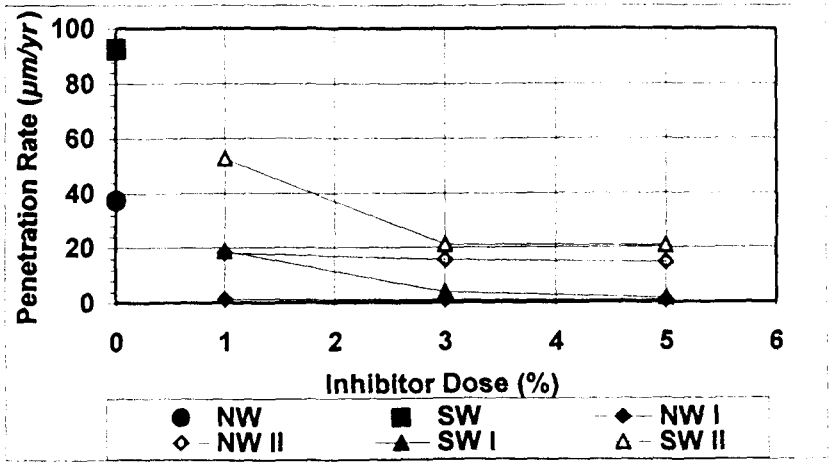
For calcium nitrite and tannic acid, the effect of exposure duration on corrosion inhibition efficiency has been presented in Table– 5.5 and Figs. 5.23 – 5.24. Calcium nitrite inhibited medium exhibits a very high corrosion inhibition efficiency in potable water medium for all the four stages of exposure duration *viz.* 30, 90, 180 and 360 *days*, however, for saline water medium for 1% dose, the efficiency reduces from 93% to 83% with the increase in exposure duration from 30 to 360 *days*.



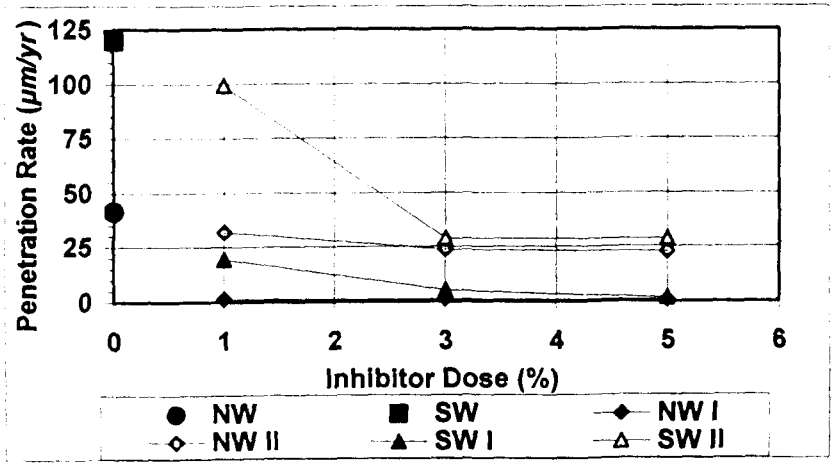
(a) 30 *days* of Exposure



(b) 90 *days* of Exposure



(c) 180 *days* of Exposure



(d) 360 *days* of Exposure

Fig. 5.22 Effect of Dose of Inhibitor on Penetration Rate for Naked Welded Steel Wire Mesh

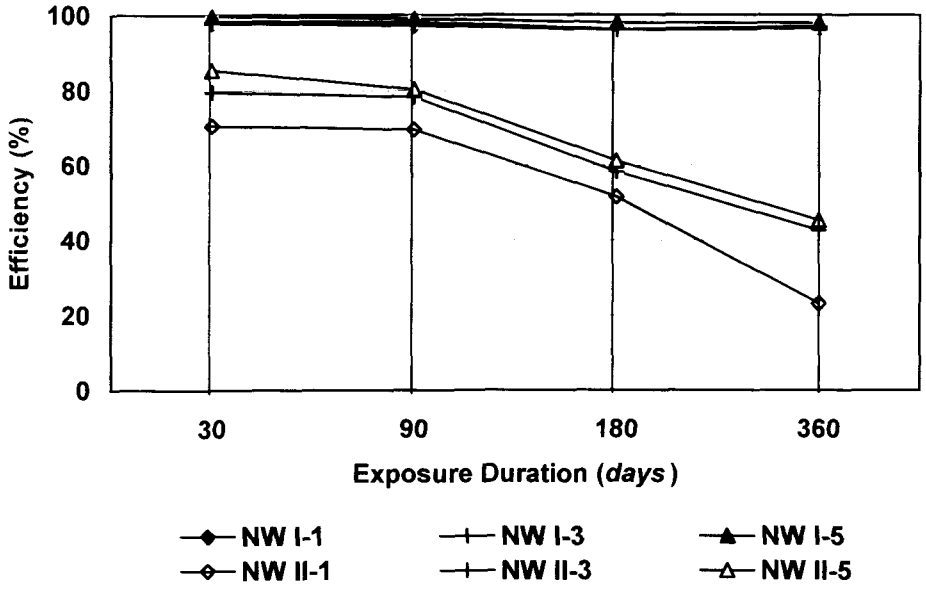


Fig. 5.23 Efficiency of Corrosion Inhibitors for Naked Welded Steel Wire Mesh in Potable Water Medium

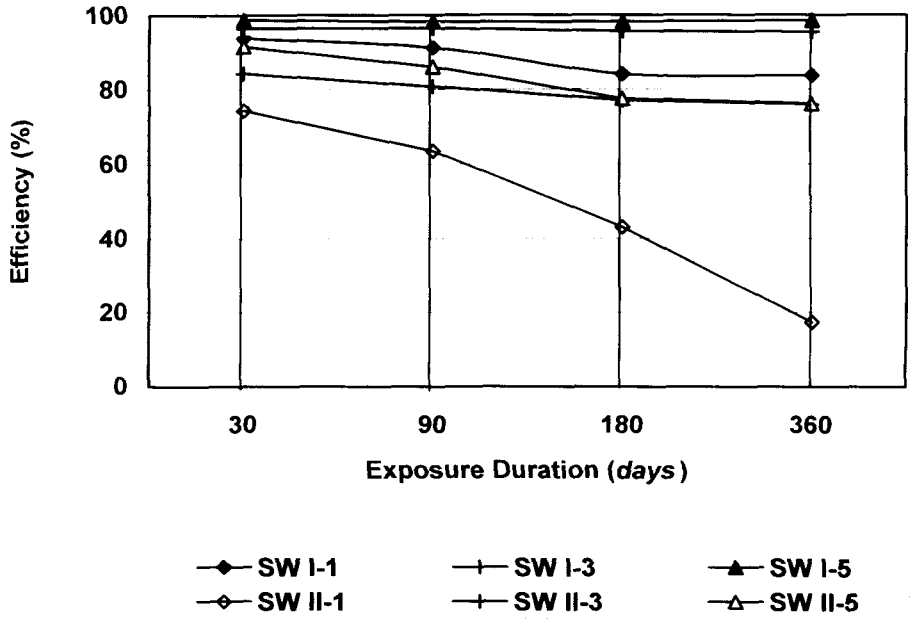


Fig. 5.24 Efficiency of Corrosion Inhibitors for Naked Welded Steel Wire Mesh in Saline Water Medium

The efficiency above 95% has been observed for 3% and 5% dose of calcium nitrite for whole duration of exposure. For the tannic acid inhibited specimen in potable water medium, the corrosion inhibition efficiency has been observed to reduce sharply for longer duration of exposure. In saline water medium, for 1% dose of tannic acid the efficiency has been found to reduce from 74% after 30 *days* of exposure to 17% after 360 *days* of exposure. However, for 3% and 5% dose of tannic acid in saline water medium, reasonably good efficiency, well above 75% is observed.

5.7.2.2 CORROSION RATE

The effect of exposure duration on the corrosion rate of naked welded steel wire mesh for calcium nitrite and tannic acid is presented in Table– 5.6 and Figs. 5.25 – 5.26. All the specimens exposed in the inhibited medium show lower corrosion rate compared to their respective uninhibited specimen exposed in the two medium of exposure (Blank-1 and Blank-2), for all exposure durations. This finding establishes the effectiveness of both the inhibitor in controlling/delaying the corrosion process. It is pertinent to mention here that, the corrosion rate has not been satisfactorily low in all the cases. Calcium nitrite inhibited solution has exhibited almost negligible corrosion rate, indicating almost passive state throughout the full exposure duration in potable water medium. In saline water medium except for the 1% dose, where the corrosion rate is little higher for longer duration of exposure, extremely good results have been observed for 3% and 5% doses. For the tannic acid inhibited specimens, the corrosion rate is found to increase with the increase in exposure duration both in potable and saline water medium. The values of corrosion rate were found to be reasonably low at higher dose and lower exposure duration but as the duration of exposure increases, the corrosion rate also increases manifold.

5.7.2.3 PENETRATION RATE

In Table– 5.6 and Figs. 5.27 – 5.28, the variation of penetration rate with the exposure duration has been presented. The effect of exposure duration on the penetration rate is similar to that observed for corrosion rate. The penetration rate remains well within the acceptable limit for calcium nitrite inhibited potable and saline water medium for all the exposure durations except for 1% dose in saline water. For the tannic acid inhibited medium, although the value of penetration rate is found to be quite high, the penetration rate remains lower than that observed for the un-inhibited medium.

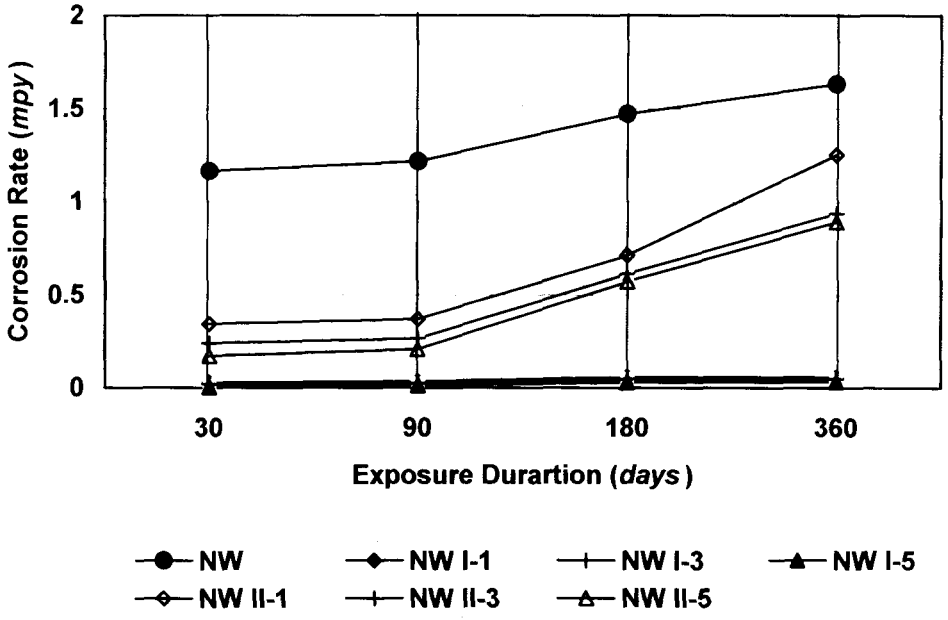


Fig. 5.25 Corrosion Rate for Naked Welded Steel Wire Mesh in Potable Water Medium

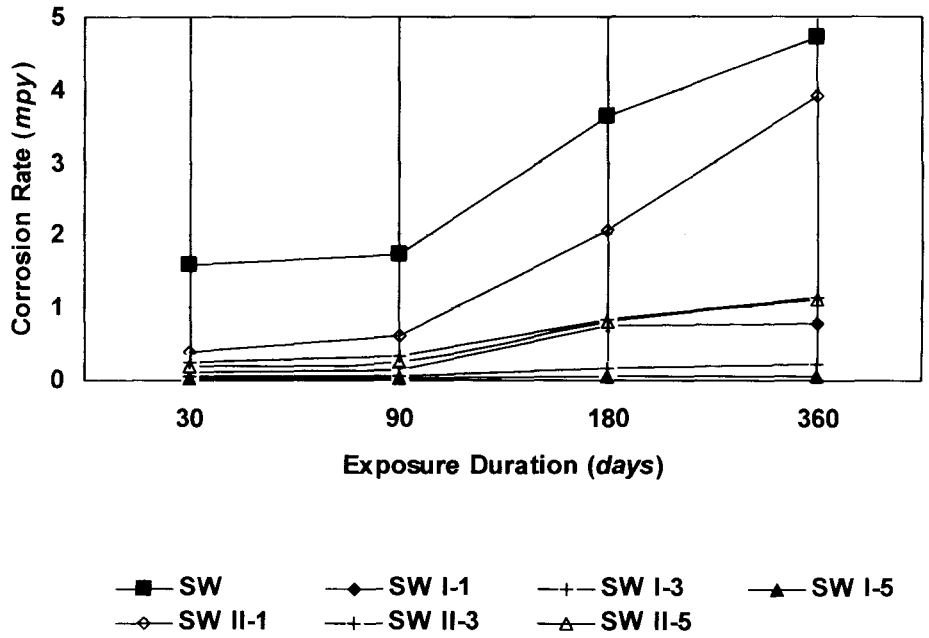


Fig. 5.26 Corrosion Rate for Naked Welded Steel Wire Mesh in Saline Water Medium

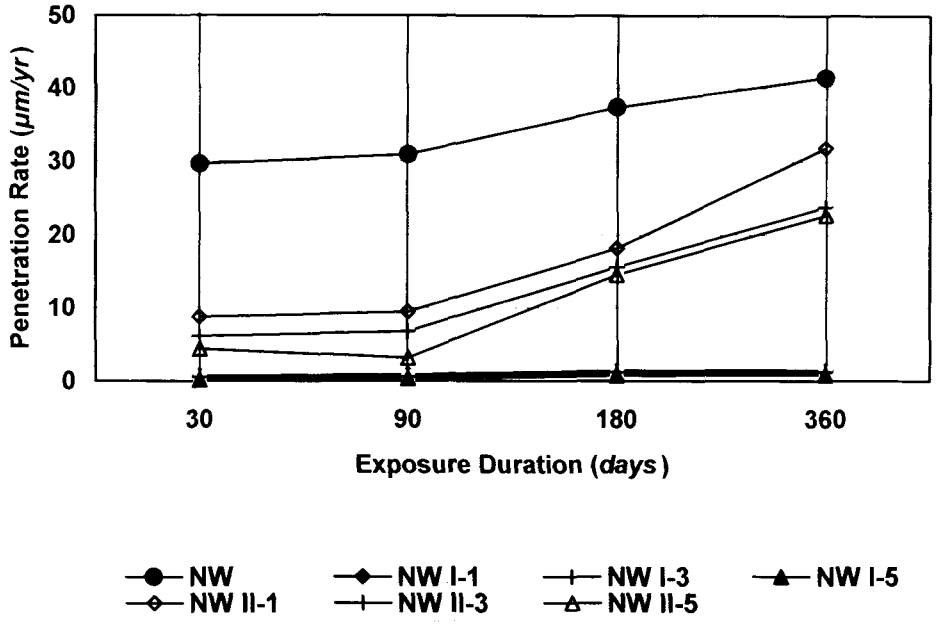


Fig. 5.27 **Penetration Rate for Naked Welded Steel Wire Mesh in Potable Water Medium**

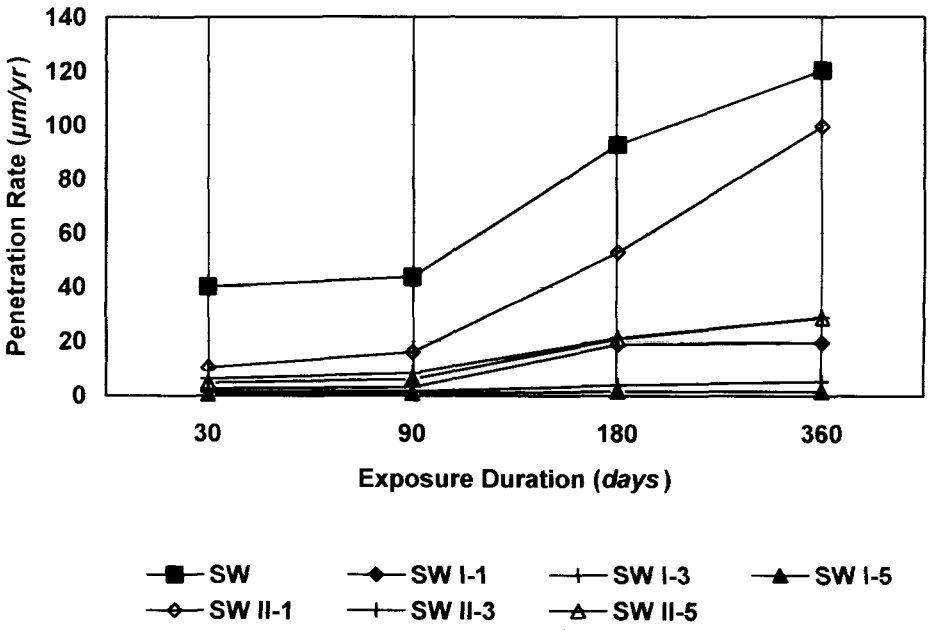


Fig. 5.28 **Penetration Rate for Naked Mild Steel Welded Wire Mesh in Saline Water Medium**

5.7.3 VISUAL INSPECTION

Some of the specimens after 360 *days* of exposure have been shown in Figs. 5.29 – 5.32. Each photograph contains one blank specimen and three inhibited specimens with a particular type and the dose of inhibitors. It has been observed that the specimens exposed in calcium nitrite inhibited potable water medium have no signs of corrosion on both the faces even at 1% dose. No trace of corrosion has also been noticed in calcium nitrite inhibited saline water medium at 5% dose of inhibitor. However, for 3% dose of calcium nitrite inhibitor in saline water medium, very nominal corrosion has been noticed. About 20% of the total surface area is observed to have undergone corrosion when the specimen is exposed in 1% calcium nitrite inhibited saline water medium.

For specimens exposed in tannic acid inhibited potable water medium, entire surface area is observed to have undergone moderate corrosion, however in saline water medium. severe corrosion is observed covering full surface of the specimen only for 1% dose of inhibitor. For 3% and 5% dose only partial surface corrosion covering about 25–40% of surface area is observed. The visual observations further validate the results presented in the previous sections.

5.7.4 MICROSCOPIC EXAMINATION

The images of naked welded steel wire mesh virgin specimen, at a magnification of 400X, along with the control and inhibited specimens after 360 *days* of exposure in different exposure medium have been shown in Figs. 5.33 – 5.34.

In the Figs. 5.33(a) and 5.34(a), the magnified image of naked welded steel wire mesh virgin specimen has been shown which shows the corrosion free surface of the specimen. The naked welded steel wire mesh virgin specimen exposed in blank potable water medium after 360 *days* of exposure duration has been shown in Fig. 5.33(b) where the effect of corrosion action can be easily seen. The naked welded steel wire mesh virgin specimen inhibited with 1% calcium nitrite has been shown in Fig. 5.33(c) where little corrosion activity can be viewed. In the Fig. 5.33(d), the naked welded steel wire mesh virgin specimen with 5% calcium nitrite has been shown wherein the inhibitors play its effective role and thus completely forbidding the corrosion activity.

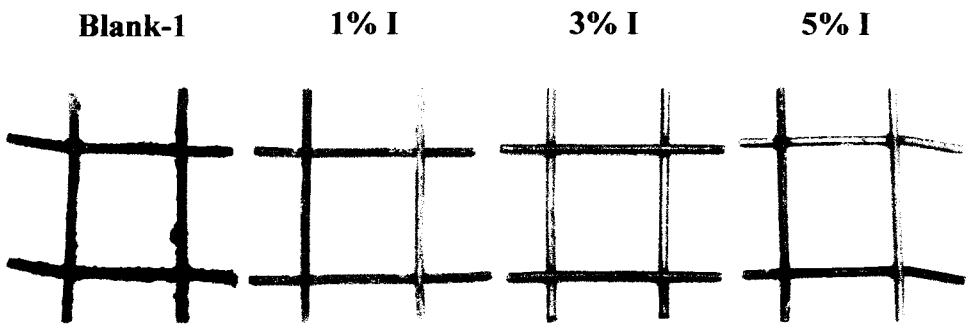


Fig. 5. 29 Naked Welded Steel Wire Mesh Specimen after 360 *days* of Exposure in Potable Water Medium (Blank and Calcium Nitrite Inhibited)

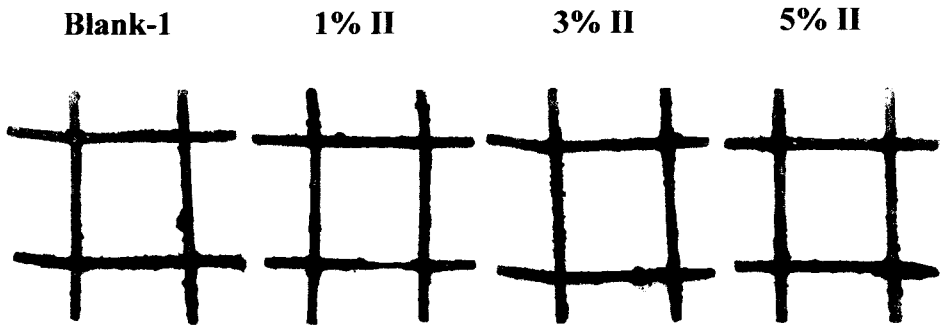


Fig. 5. 30 Naked Welded Steel Wire Mesh Specimen after 360 *days* of Exposure in Potable Water Medium (Blank and Tannic Acid Inhibited)

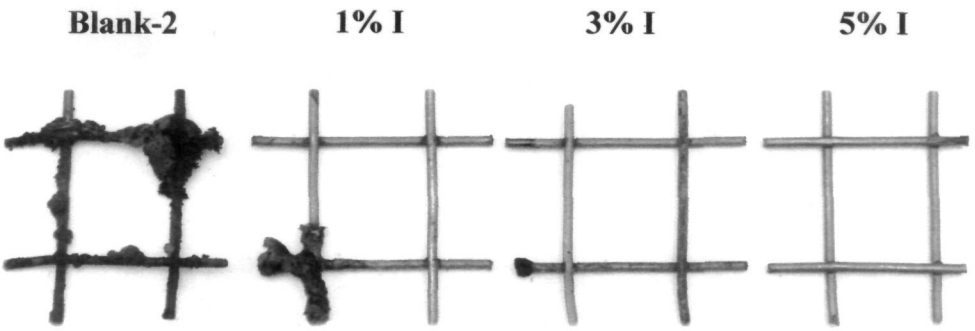


Fig. 5. 31 **Naked Welded Steel Wire Mesh Specimen after 360 *days* of Exposure in Saline Water Medium (Blank and Calcium Nitrite Inhibited)**

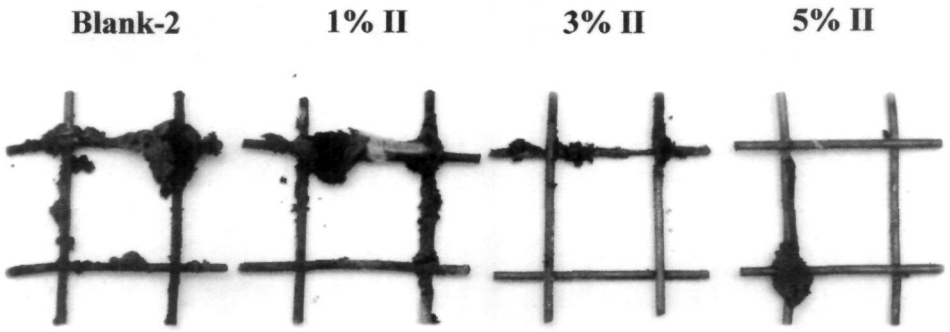
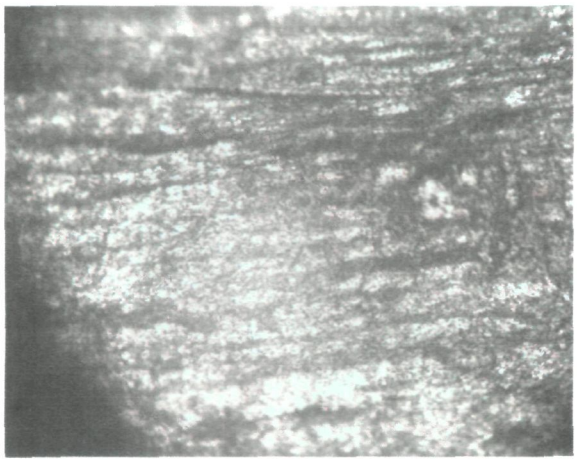
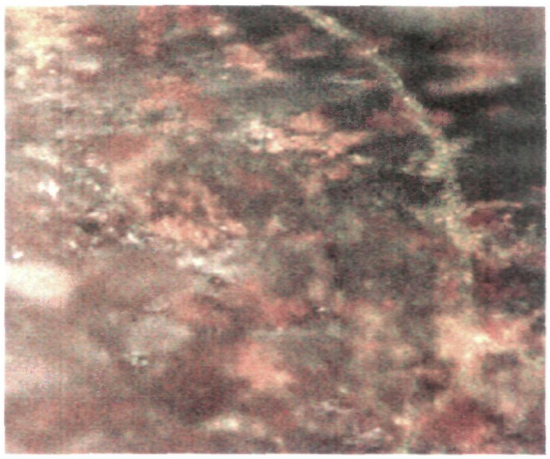


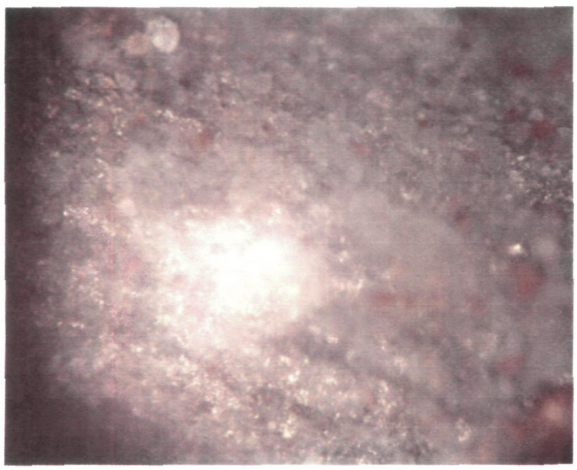
Fig. 5. 32 **Naked Welded Steel Wire Mesh Specimen after 360 *days* of Exposure in Saline Water Medium (Blank and Tannic Acid Inhibited)**



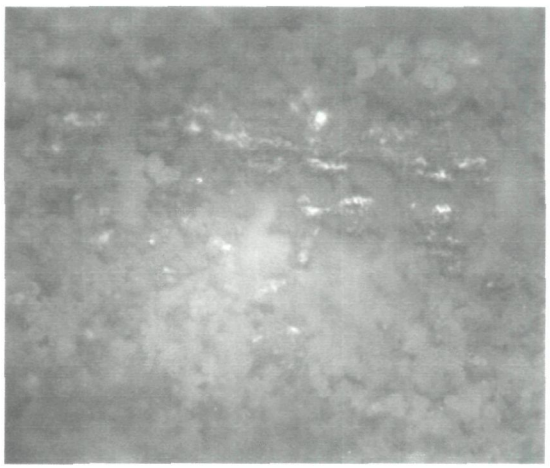
(a) Virgin Wire Mesh Specimen



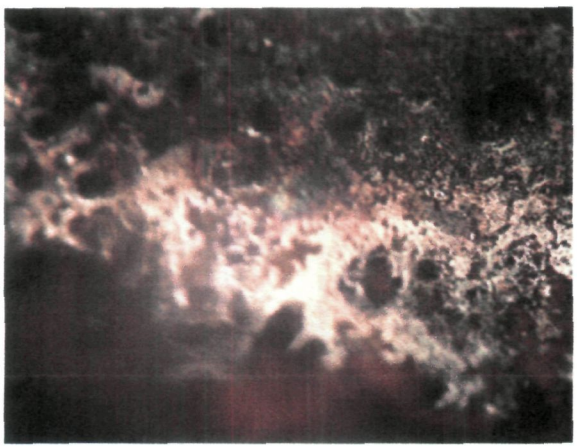
(b) Blank-1 (Potable Water)



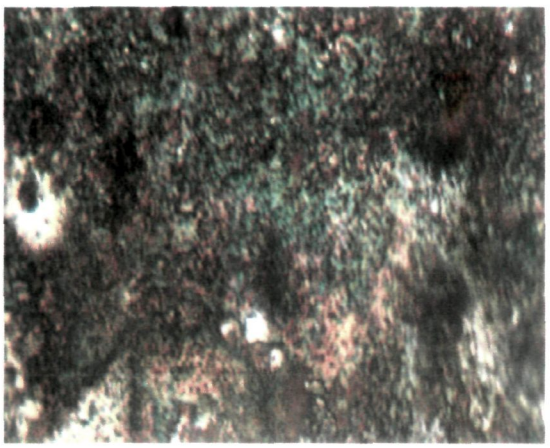
(c) 1% Calcium Nitrite



(d) 5% Calcium Nitrite

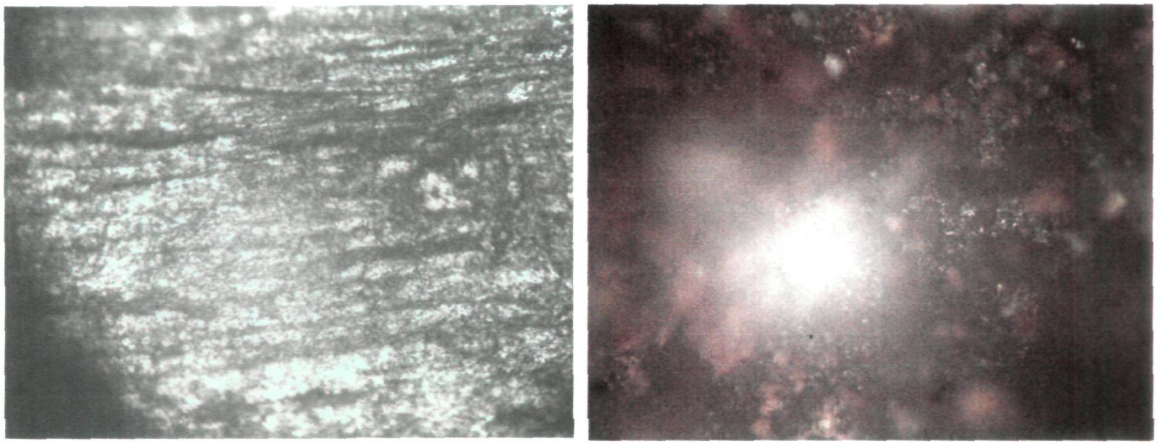


(e) 1% Tannic Acid

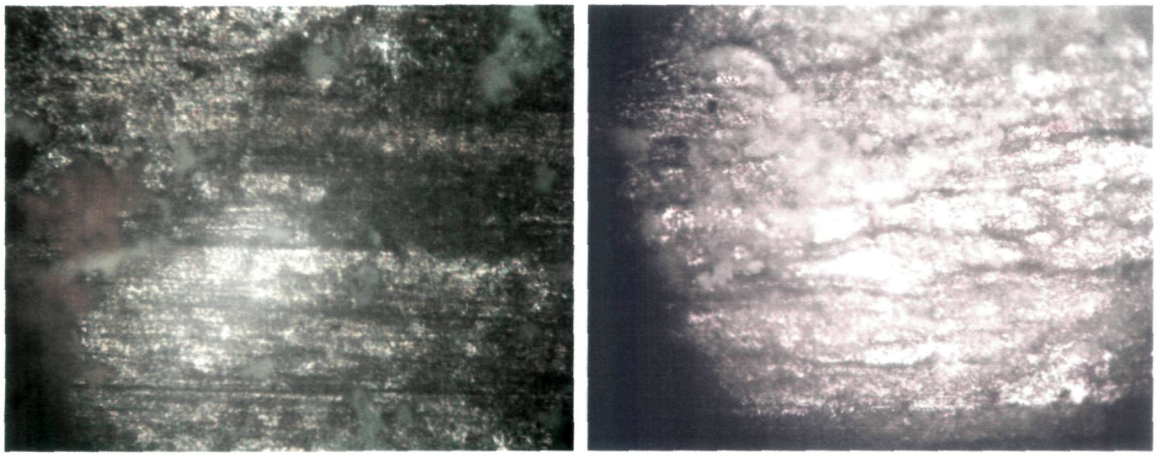


(f) 5% Tannic Acid

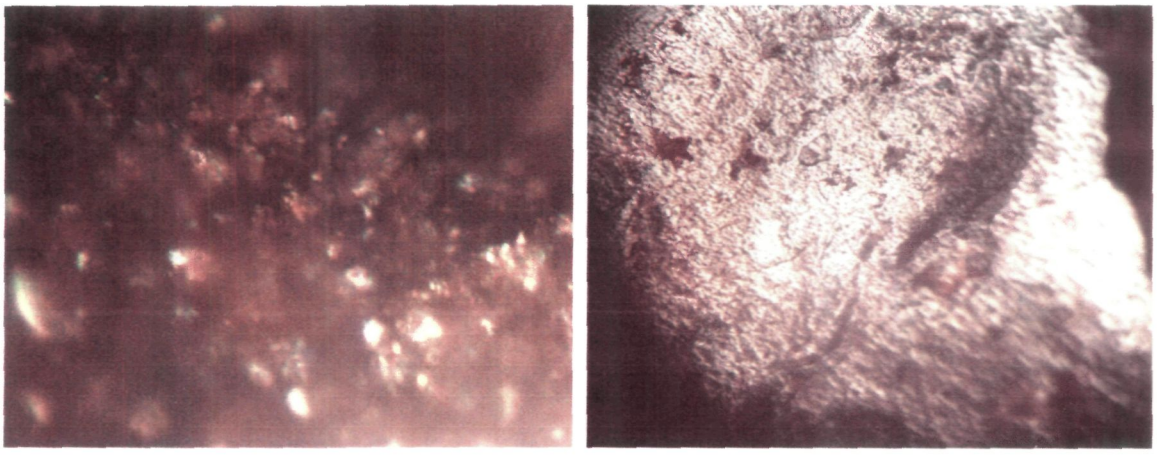
Fig. 5.33 Microscopic Images at 400X Magnification of Naked Welded Steel Wire Mesh Specimen after 360 *days* of Exposure in Potable Water Medium



(a) Virgin Wire Mesh Specimen (b) Blank-2 (Saline Water)



(c) 1% Calcium Nitrite (d) 5% Calcium Nitrite



(e) 1% Tannic Acid (f) 5% Tannic Acid

Fig. 5.34 Microscopic Images at 400X Magnification of Naked Welded Steel Wire Mesh Specimen Specimens after 360 *days* of Exposure in Saline Water Medium

For specimens exposed in tannic acid inhibited potable water medium, entire surface area is observed to have undergone moderate corrosion as may be seen in Figs. 5.33(e) and 5.33(f).

The naked welded steel wire mesh virgin specimen exposed in blank saline water medium after 360 *days* of exposure duration has been shown in Fig. 5.34(b) where the entire specimen surface undergoes corrosion. The naked welded steel wire mesh virgin specimen inhibited with 1% calcium nitrite has been shown in Fig. 5.34(c) where the corrosion activity spread over 20% of surface area can be viewed. In the Fig. 5.34(d), the naked welded steel wire mesh virgin specimen with 5% calcium nitrite has been shown wherein mild corrosion activity has been noticed which further validates the merits of corrosion inhibitor. Tannic acid, however, continues to be ineffective in controlling corrosion both at 1% dose and of 5% as may be seen in Figs. 5.34(e) and 5.34(f) where the corrosion activity appears to be in full bloom.

It is further evident that calcium nitrite is far more effective in preventing corrosion even at 1% concentration in potable water medium; however a mild corrosion has been observed at this concentration in saline water medium. With higher dose a still higher inhibition is observed both in saline and potable water medium. Tannic acid is not found to be so effective in mitigating corrosion. Similar results were obtained in the gravimetric weight loss analysis and visual inspection of the specimens.

5.8 TESTS ON CEMENT SLURRY COATED WELDED STEEL WIRE MESH SPECIMENS

After recording their initial weight, the cement slurry coated welded steel wire mesh specimens, as shown in Fig. 5.3, were exposed to the different mediums as per the scheme shown in Table– 5.1. After the completion of specified time of exposure, the specimens were taken out of the medium, cleaned and dried. The final weight of the specimen was then recorded. Using the weight loss, corrosion inhibition efficiency, corrosion rate and penetration rate were calculated as per Eqns. 5.1–5.3. The results have been given in Tables– 5.7 and 5.8 and shown in Figs. 5.35 – 5.43. The tested cement slurry coated welded steel wire mesh specimens after 360 *days* of exposure under different mediums are shown in Figs. 5.44 – 5.47.

5.8.1 EFFECT OF INHIBITOR DOSE

The dose of the inhibitors was varied as 1%, 3% and 5% for both calcium nitrite and tannic acid. The effect of the variation of the dose of corrosion inhibitors on corrosion inhibition efficiency, corrosion rate and penetration rate has been discussed in the following sub-sections.

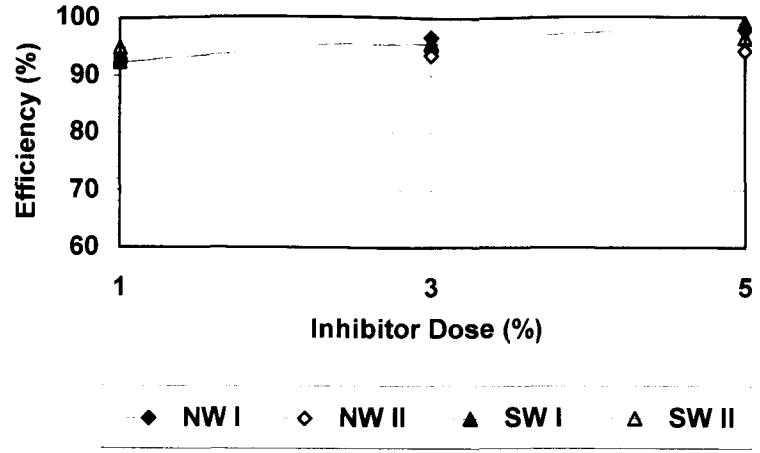
5.8.1.1 CORROSION INHIBITION EFFICIENCY

The corrosion inhibition efficiency exhibited by the calcium nitrite and tannic acid for the cement slurry coated welded steel wire mesh specimens is given in Table– 5.7 and Figs. 5.35(a-d). The corrosion inhibition efficiency is found to increase substantially when the dose of calcium nitrite is increased from 1% to 3%. With further increase in the dose to 5%, only a marginal increase in the corrosion inhibition efficiency is observed. This observation holds equally, both for potable and saline water medium at all the exposure durations. Extremely high efficiency has been observed for all the doses of calcium nitrite. Even at 1% dose of inhibitor, the efficiency was found to be around 90% in both potable and saline water medium, except after 180 *days* and 360 *days* of exposure in saline water medium where a reasonably good efficiency, well above 75%, is observed.

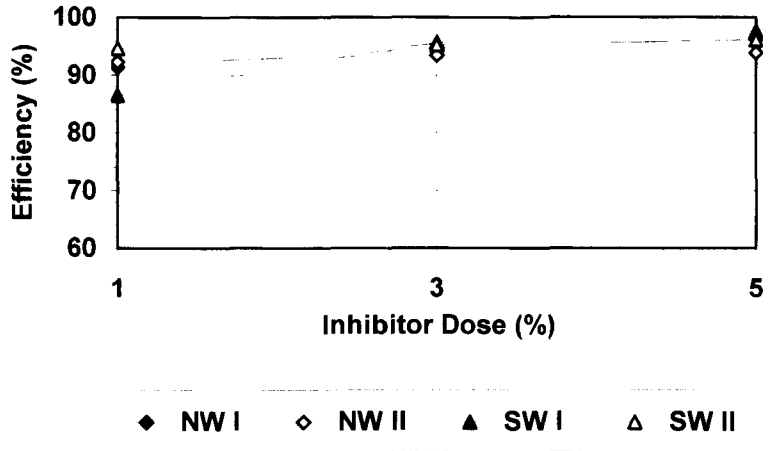
Contrary to the results obtained for mild steel plate and naked steel wire mesh specimens, the level of efficiency exhibited by the tannic acid has been comparable to the calcium nitrite for the cement slurry coated welded steel wire mesh specimens. A reasonably high efficiency of the order of 92% and 94% has been observed respectively in potable and saline water medium, even for 1% dose of inhibitor. With further increase in the dose of the inhibitor, only a marginal increase in corrosion inhibition efficiency has been observed both in potable and saline water medium. The reason behind tannic acid being so effective in controlling corrosion in cement slurry coated specimen is perhaps the protection provided to the tannic film formed over the metal surface. Coating of cement slurry applied over the tannic acid film possibly protects it from getting dissolved in aqueous solution with the passage of time.

Table– 5.7 Average Weight Loss and Corrosion Inhibition Efficiency for Cement Slurry Coated Welded Steel Wire Mesh

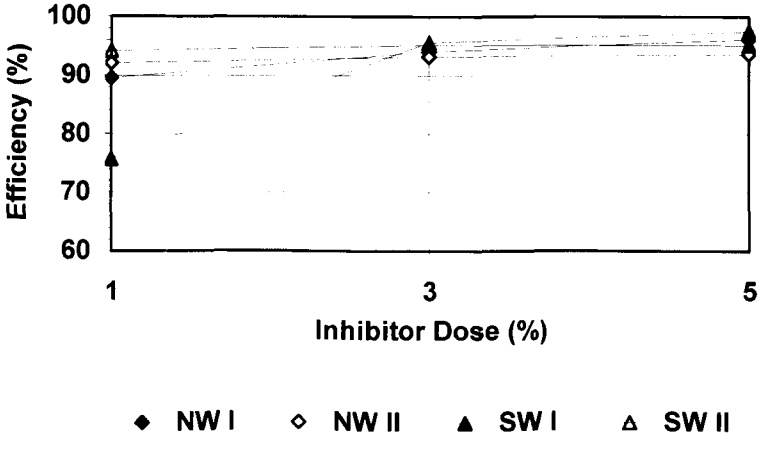
S. No.	Systems of Exposure	30 *days*		90 *days*		180 *days*		360 *days*	
		Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)
1.	NW	11.900	---	37.300	---	90.200	---	200.000	---
2.	NW I-1	0.933	92.16	3.200	91.42	8.033	91.10	21.033	89.48
3.	NW I-3	0.400	96.64	2.000	94.64	5.000	94.46	11.800	94.10
4.	NW I-5	0.267	97.77	1.433	96.16	3.333	96.30	7.800	96.10
5.	NW II-1	0.833	93.00	2.867	92.31	7.133	92.10	15.967	92.02
6.	NW II-3	0.766	93.56	2.467	93.39	6.100	93.13	13.633	93.18
7.	NW II-5	0.700	94.11	2.300	93.83	5.667	93.72	12.833	93.58
8.	SW	16.130	---	52.667	---	223.000	---	579.300	---
9.	SW I-1	1.233	92.36	7.100	86.52	57.967	74.00	140.133	75.81
10.	SW I-3	0.700	95.66	2.130	95.59	9.800	95.60	25.667	95.56
11.	SW I-5	0.167	98.96	1.233	97.65	7.500	96.64	14.410	97.51
12.	SW I-1	0.833	94.84	2.800	94.68	11.867	94.68	33.667	94.19
13.	SW II-3	0.733	95.46	2.500	95.25	10.367	95.35	28.533	95.10
14.	SW II-5	0.567	96.48	2.033	96.14	9.600	95.69	27.967	95.17



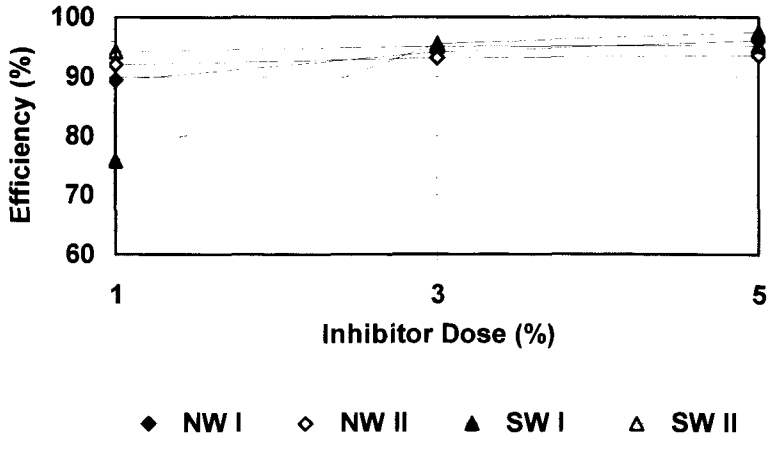
(a) 30 *days* of Exposure



(a) 90 *days* of Exposure



(a) 180 *days* of Exposure



(a) 360 *days* of Exposure

Fig. 5.35 Effect of Dose of Inhibitor on Corrosion Inhibition Efficiency for Cement Slurry Coated Welded Steel Wire Mesh

5.8.1.2 CORROSION RATE

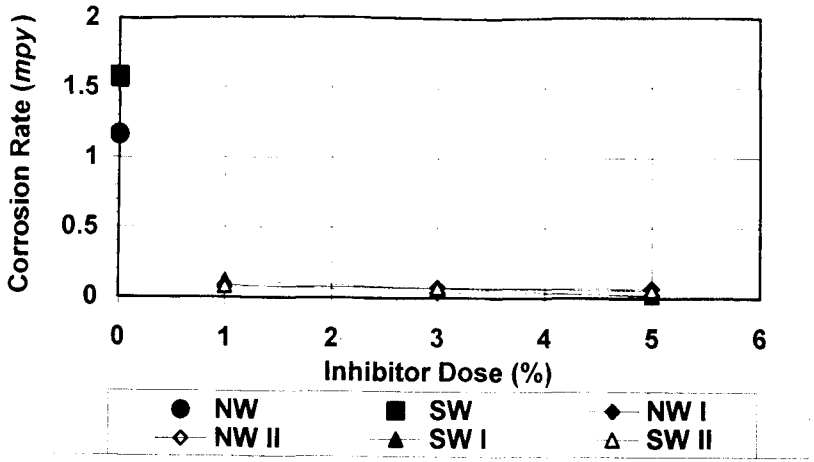
For the cement slurry coated welded steel wire mesh specimens, the corrosion rate have been presented in Table– 5.8 and Figs. 5.36(a-d). In potable water medium without corrosion inhibitor (Blank-1), the corrosion rate has been found to be lower than the corrosion rate in saline water medium without corrosion inhibitor (Blank-2). Calcium nitrite inhibitor exhibited extremely low corrosion rate for all the doses in potable water medium throughout the exposure duration. The specimens were observed to be almost in complete passive state even after 360 *days* of exposure. In saline water medium, similar trend has been observed except for the 1% dose of calcium nitrite after 180 and 360 *days* of exposure, where a relatively higher corrosion rate has been found. Tannic acid also exhibits a low corrosion rate similar to that exhibited by calcium nitrite. Both in potable water and saline water medium, for all the doses of inhibitors, the corrosion rate has been found to be limited to a very low value, clearly indicating a very high degree of inhibition. No significant change in corrosion rate is noticed with the increase in the dose of tannic acid especially in potable water medium.

5.8.1.3 PENETRATION RATE

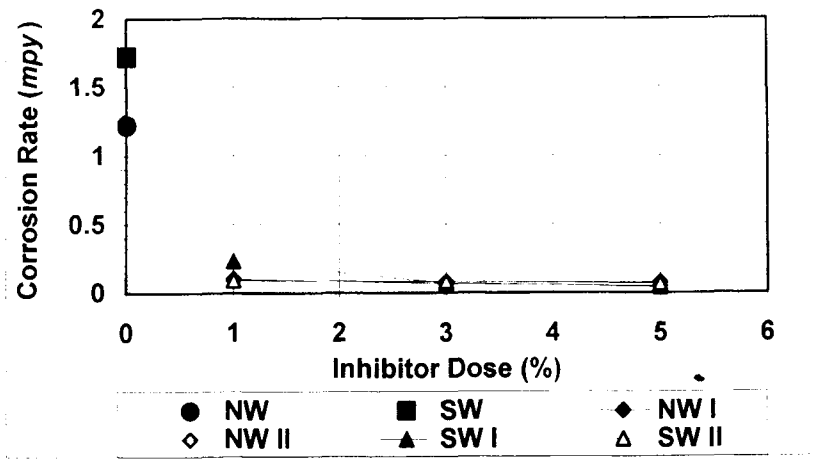
The penetration rate has been presented in Table– 5.8 and Figs. 5.37(a-d). The values of penetration rate impart extremely satisfactory results both for calcium nitrite, and tannic acid especially in potable water medium. In saline water medium, excellent corrosion inhibition efficiency has been shown by both calcium nitrite and tannic acid at 3% and 5% dose of inhibitor. Calcium nitrite with 1% dose in saline water does not perform well for longer duration of exposure, thereby, resulting in higher values of penetration rate. For tannic acid in saline water medium, the penetration rate values at 1% dose are found to be slightly above the penetration rate range specified for passive to mild state of corrosion (2–6 *μm/year*), whereas for 3% and 5% dose of tannic acid inhibitor, the penetration rate values are well within this range.

Table– 5.8 Corrosion Rate and Penetration rate for Cement Slurry Coated Welded Steel Wire Mesh

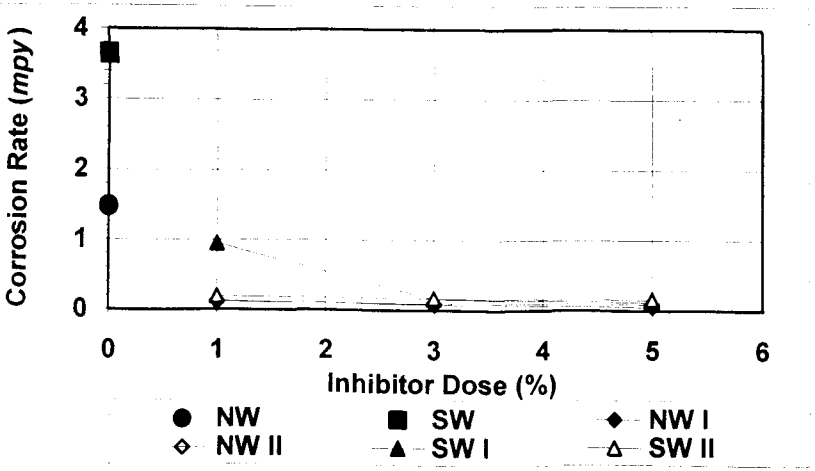
S. No.	Systems of Exposure	30 *days*		90 *days*		180 *days*		360 *days*	
		Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)
1.	NW	1.166	29.616	1.219	30.963	1.473	37.414	1.633	41.472
2.	NW I-1	0.091	2.311	0.104	2.642	0.131	3.327	0.172	4.369
3.	NW I-3	0.039	0.991	0.065	1.651	0.082	2.083	0.096	2.438
4.	NW I-5	0.026	0.660	0.047	1.194	0.054	1.372	0.064	1.626
5.	NW II-1	0.082	2.080	0.094	2.390	0.116	2.950	0.130	3.302
6.	NW II-3	0.075	1.905	0.081	2.057	0.100	2.540	0.111	2.820
7.	NW II-5	0.069	1.753	0.075	1.905	0.093	2.362	0.105	2.667
8.	SW	1.581	40.157	1.721	43.713	3.643	92.532	4.731	120.167
9.	SW I-1	0.121	3.073	0.232	5.893	0.947	24.054	1.144	29.058
10.	SW I-3	0.069	1.753	0.070	1.778	0.160	4.060	0.210	5.334
11.	SW I-5	0.016	0.410	0.040	1.016	0.122	3.100	0.188	3.000
12.	SW I-1	0.082	2.083	0.091	2.311	0.194	4.930	0.275	6.985
13.	SW II-3	0.072	1.829	0.082	2.083	0.169	4.293	0.233	5.918
14.	SW II-5	0.055	1.397	0.066	1.676	0.157	3.988	0.228	5.791



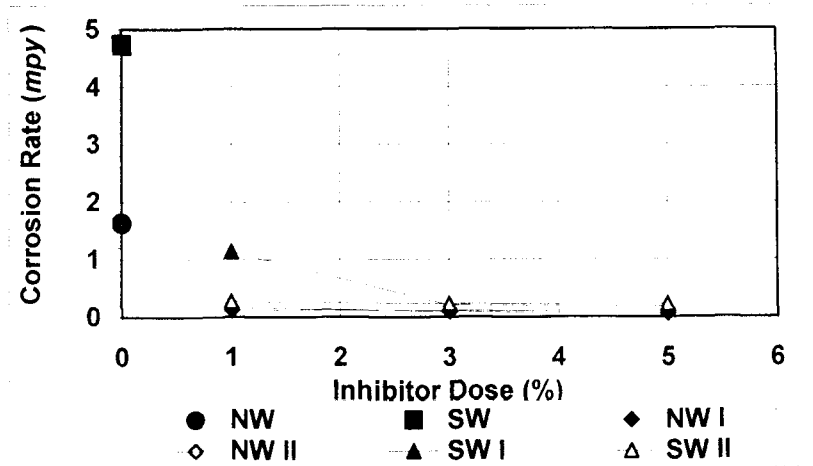
(a) 30 *days* of Exposure



(a) 90 *days* of Exposure

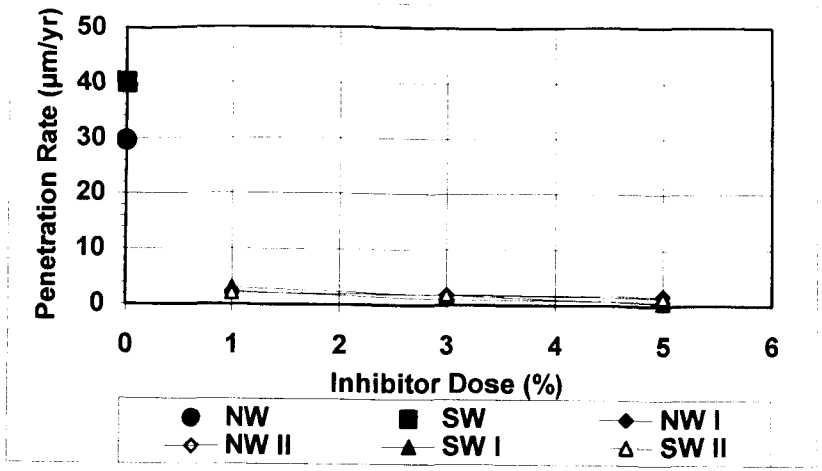


(a) 180 *days* of Exposure



(a) 360 *days* of Exposure

Fig. 5.36 Effect of Dose of Inhibitor on Corrosion Rate for Cement Slurry Coated Welded Steel Wire Mesh



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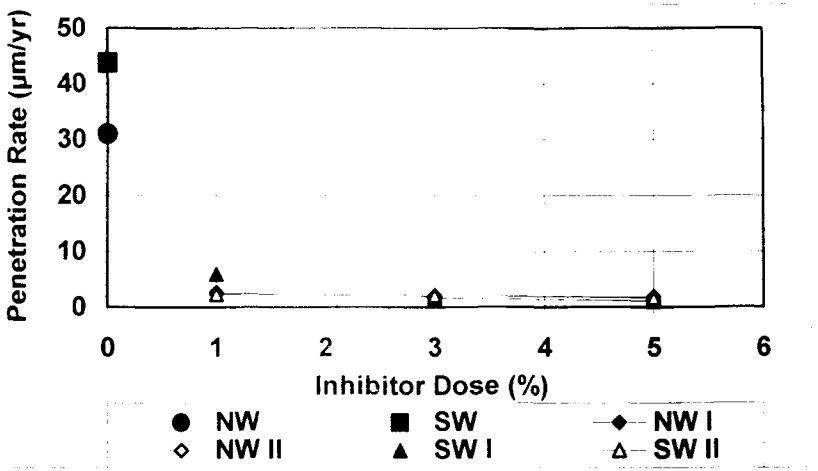
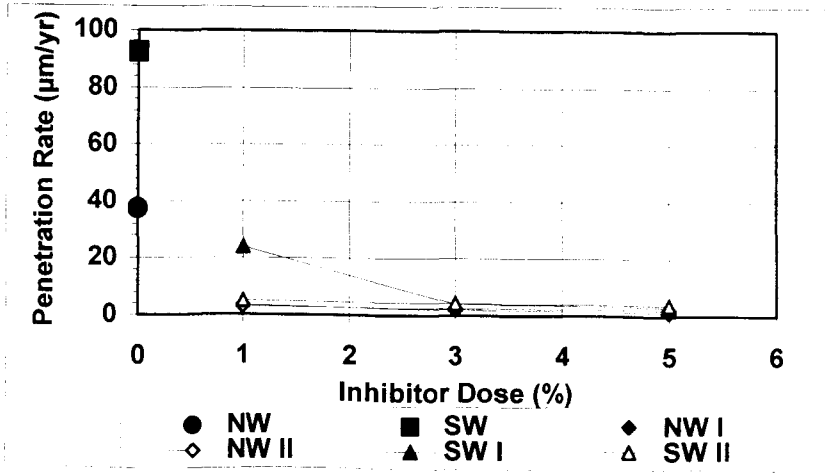
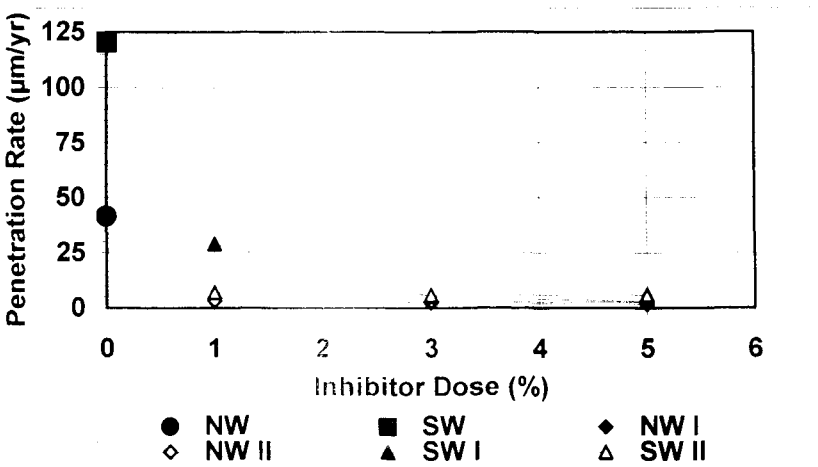


(a) 90 *days* of Exposure



(a) 180 *days* of Exposure



(a) 360 *days* of Exposure

Fig. 5.37 Effect of Dose of Inhibitor on Penetration Rate for Cement Slurry Coated Welded Steel Wire Mesh

5.8.2 EFFECT OF EXPOSURE DURATION

For the cement slurry coated welded steel wire mesh specimen, the effect of the exposure duration on corrosion inhibition efficiency, corrosion and penetration rate is being presented in the following sub-sections. The specimens were exposed for 30, 90, 180 and 360 *days*.

5.8.2.1 CORROSION INHIBITION EFFICIENCY

The variation in corrosion inhibition efficiency with exposure duration has been presented in Table– 5.7 and Figs. 5.38 – 5.39. It has been observed that with the increase in exposure duration the corrosion inhibition efficiency reduces only marginally both in potable and saline water medium. Very high corrosion inhibition efficiency is observed for both calcium nitrite and tannic acid in potable water medium throughout the period of exposure. A similar trend in saline water medium has also been noticed except for the 1% dose of the calcium nitrite. The value of corrosion inhibition efficiency remains more than 90% in majority of the specimen groups except for the 1% dose of the calcium nitrite where it reduces to 75% for longer duration of exposure. In contrast to the observations made in case of mild steel plate and naked welded steel wire mesh, tannic acid exhibits very high corrosion inhibition efficiency for cement slurry coated wire mesh specimen. As explained in previous section, the reason may be attributed to the protection of the tannic acid coating by the cement slurry cover, applied over the specimen. In the presence of the cement slurry cover, the dissolution of the tannic acid coating is prevented to a greater extent.

5.8.2.2 CORROSION RATE

The variation of corrosion rate with exposure duration has been presented in Table– 5.8 and Figs. 5.40 – 5.41. Very high corrosion rate has been observed in case of uninhibited specimens exposed to saline water medium (Blank-2), as compared to potable water medium (Blank-1) and all the other corrosion inhibited specimen groups. This observation holds for all the four stages of exposure durations. The corrosion rate either remains the same or increases marginally with the increase in exposure duration.

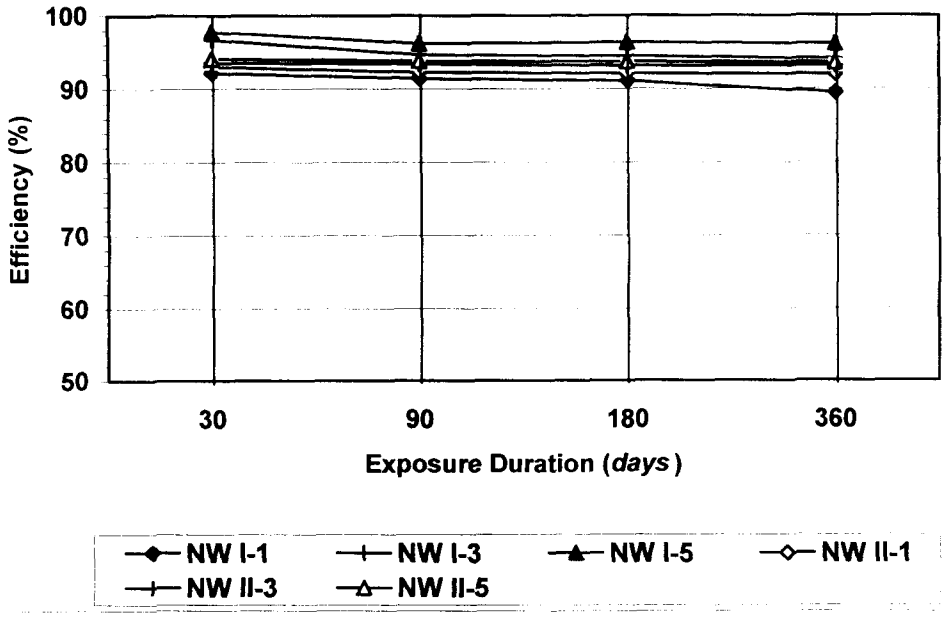


Fig. 5.38 **Efficiency of Corrosion Inhibitors for Cement Slurry Coated Welded Steel Wire Mesh in Potable Water Medium**

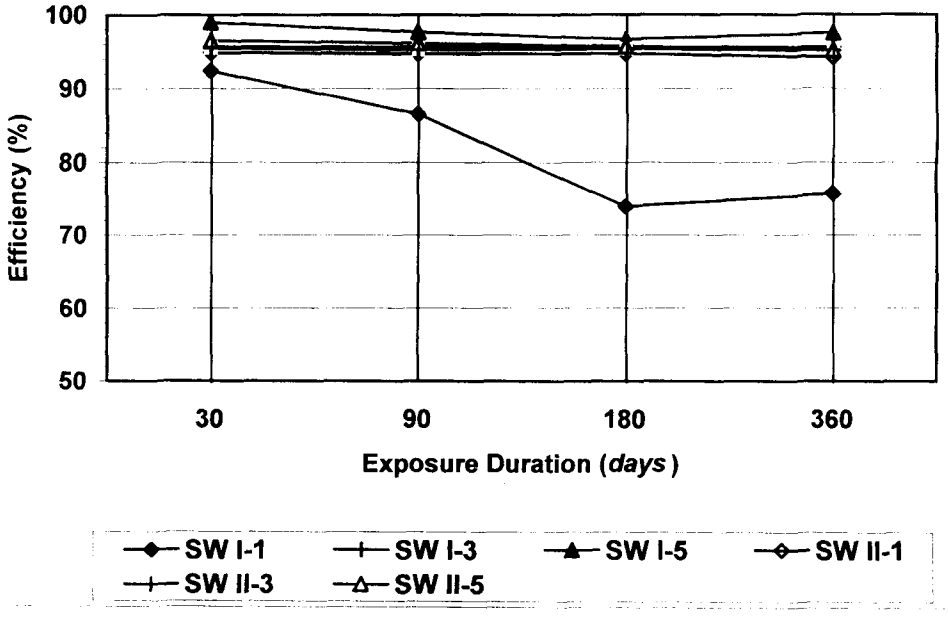


Fig. 5.39 **Efficiency of Corrosion Inhibitors for Cement Slurry Coated Welded Steel Wire Mesh in Saline Water Medium**

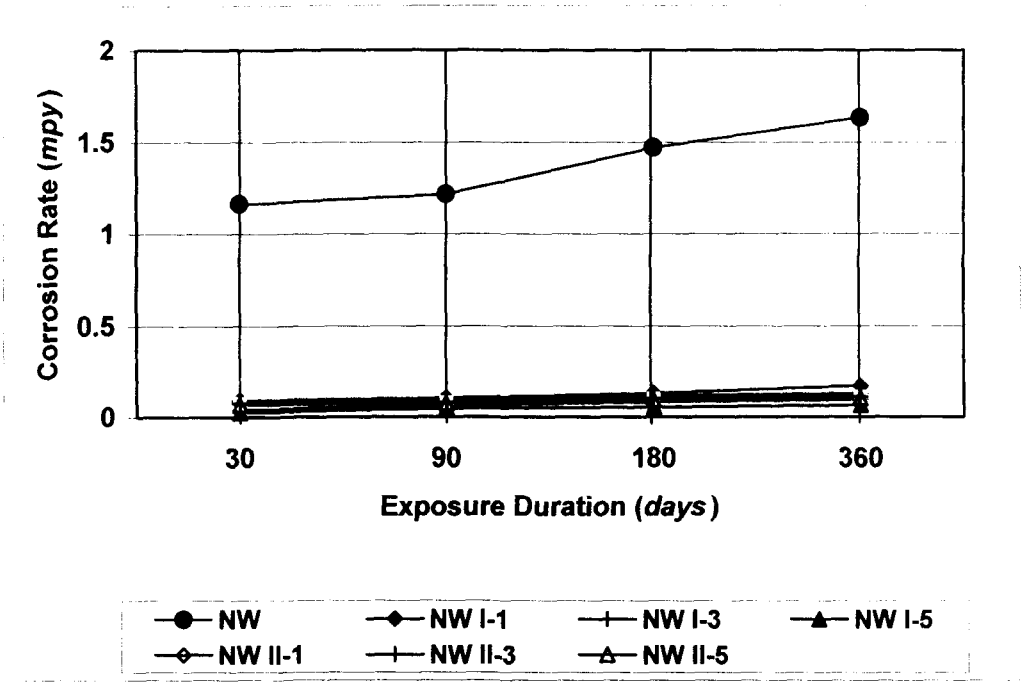


Fig. 5.40 Corrosion Rate for Cement Slurry Coated Welded Steel Wire Mesh in Potable Water Medium

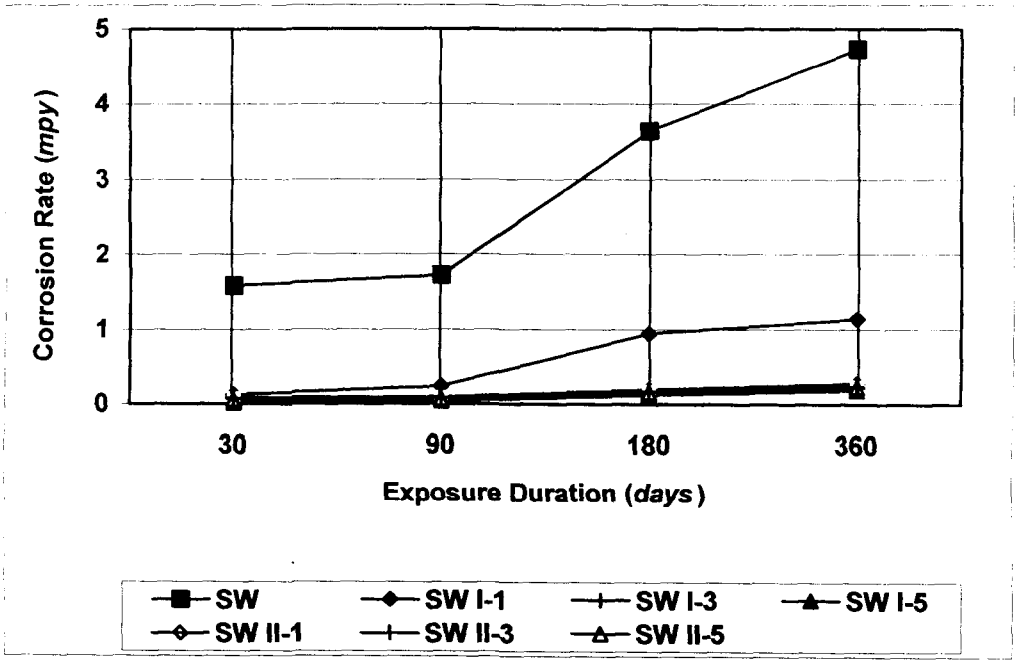


Fig. 5.41 Corrosion Rate for Cement Slurry Coated Mild Steel Welded Wire Mesh in Saline Water Medium

Except for the 1% dose of the calcium nitrite, where the corrosion rate is high for the longer duration of the exposure, exceptionally low corrosion rate has been observed for all other specimens for both the inhibitors.

5.8.2.3 PENETRATION RATE

The effect of variation of exposure duration on penetration rate has been presented in Table– 5.8 and Figs. 5.42 – 5.43. A similar trend as that of corrosion rate has been observed in case of penetration rate also. The penetration rate remains well within the acceptable limit for calcium nitrite inhibited medium for whole of the exposure duration except for the 1% dose in saline water medium. For the tannic acid inhibited specimens very low penetration has been observed even for 1% dose, both in potable and saline water medium.

5.8.3 VISUAL INSPECTION

Some of the cement slurry coated welded steel wire mesh specimens after 360 *days* of exposure have been shown in Figs. 5.44 – 5.47. As explained earlier, here also each photograph contains one blank specimen and three inhibited specimens with varying dose of inhibitors. For the Blank-1 specimen, high surface corrosion covering complete surface area has been observed. For the Blank-2 specimen, severe corrosion covering full surface has been noticed. It has been observed that the specimen exposed in calcium nitrite inhibited potable water medium, has no sign of corrosion for 5% dose. For 3% dose, only one or two spots of corrosion and for 1% dose only some localized spots can be seen. Non traceable to a very few isolated spots of corrosion have also been noticed in calcium nitrite inhibited saline water medium at 3% and 5% dose of inhibitor. However, for 1% dose of calcium nitrite inhibitor in saline water medium, mild surface corrosion, spread over almost 40-50% of the surface area, is observed.

In case of specimens exposed in tannic acid inhibited potable water medium, only some spots of corrosion are found for all the three doses. In saline water medium, slightly more spots of corrosion as compared to that found in potable water medium are observed. The visual observations therefore validate the findings presented in the previous sections.

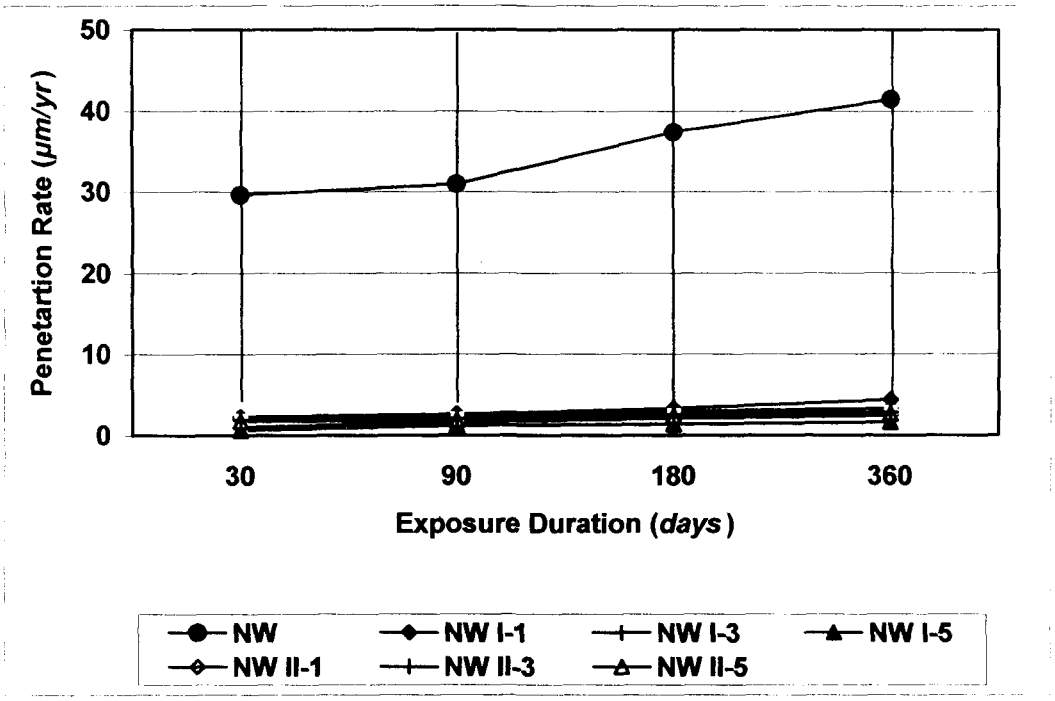


Fig. 5.42 Penetration Rate for Cement Slurry Coated Welded Steel Wire Mesh in Potable Water Medium

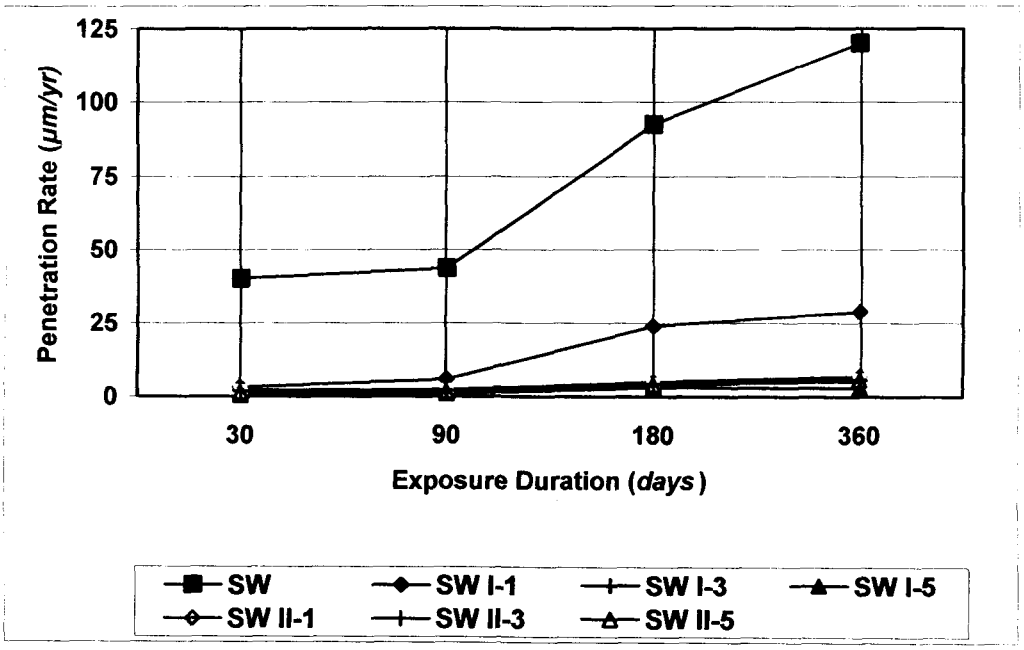


Fig. 5.43 Penetration Rate for Cement Slurry Coated Welded Steel Wire Mesh in Saline Water Medium

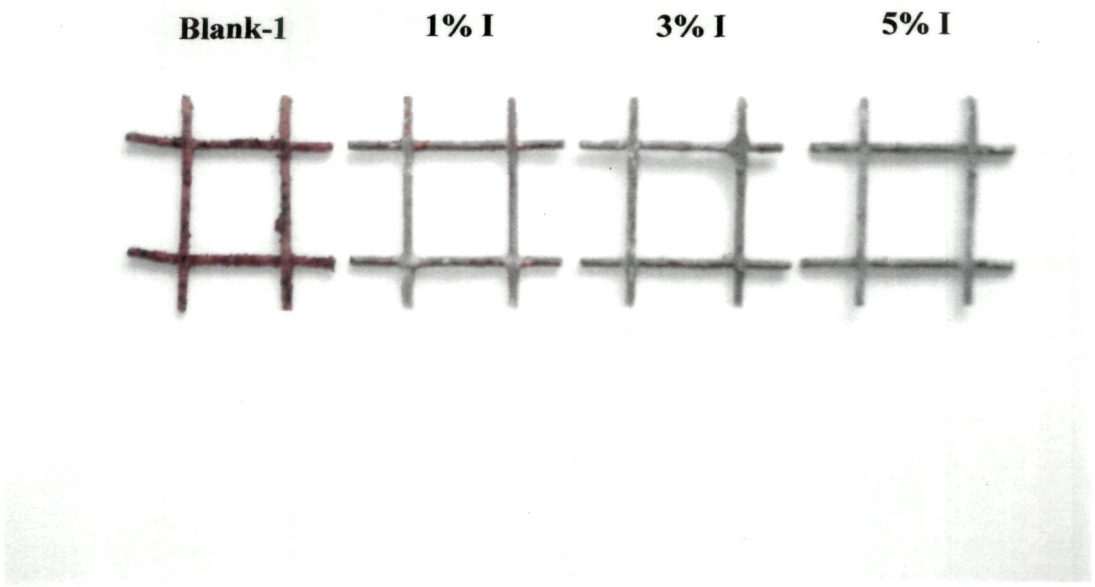


Fig. 5.44 **Cement Slurry Coated Welded Steel Wire Mesh Specimen after 360 *days* of Exposure in Potable Water Medium (Blank and Calcium Nitrite Inhibited)**

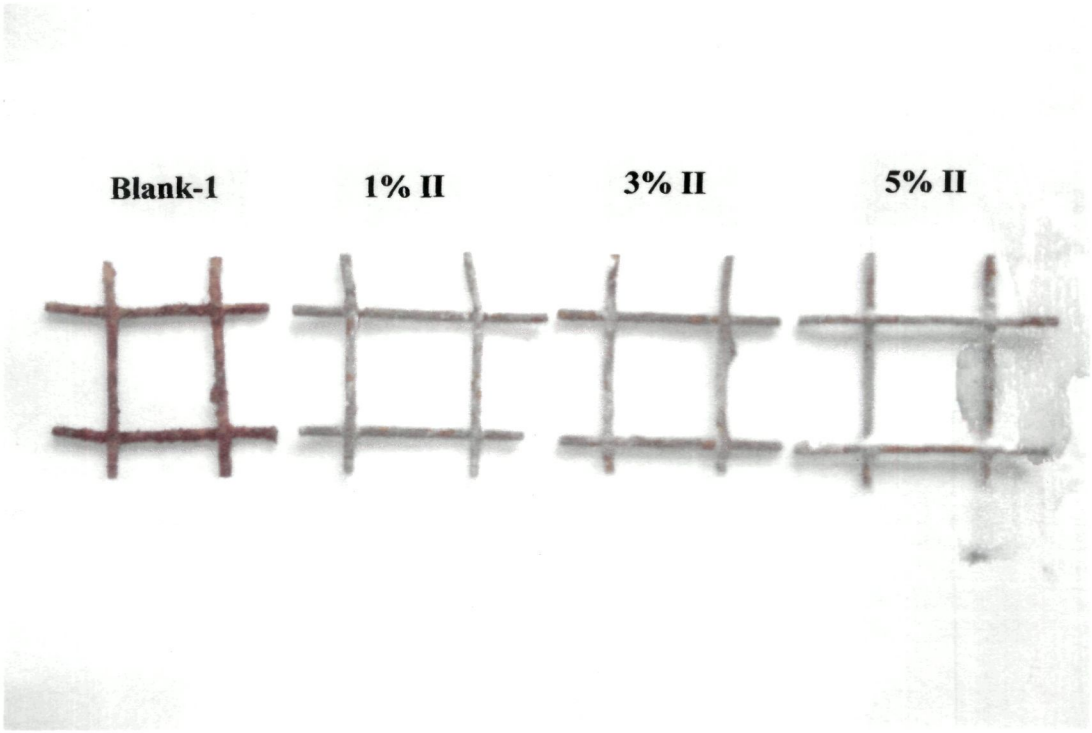


Fig. 5.45 **Cement Slurry Coated Welded Steel Wire Mesh Specimen after 360 *days* of Exposure in Potable Water Medium (Blank and Tannic Acid Inhibited)**

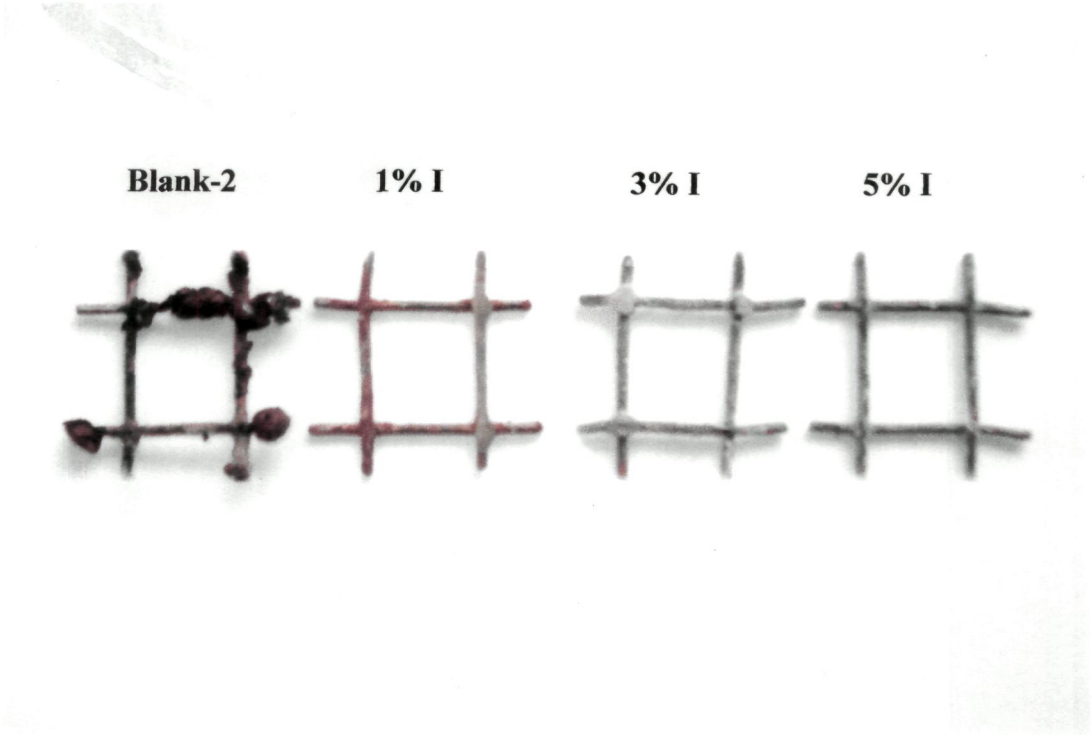


Fig. 5.46 **Cement Slurry Coated Welded Steel Wire Mesh Specimen after 360 *days* of Exposure in Saline Water Medium (Blank and Calcium Nitrite Inhibited)**

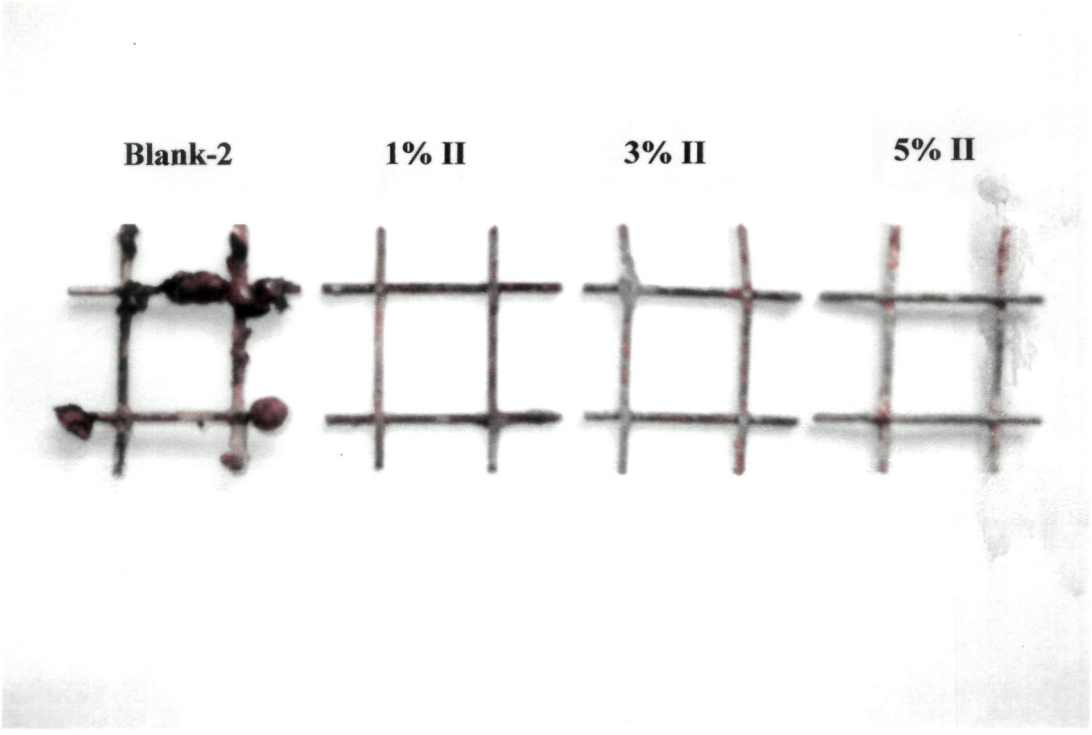


Fig. 5.47 **Cement Slurry Coated Welded Steel Wire Mesh Specimen after 360 *days* of Exposure in Potable Water Medium (Blank and Tannic Acid Inhibited)**

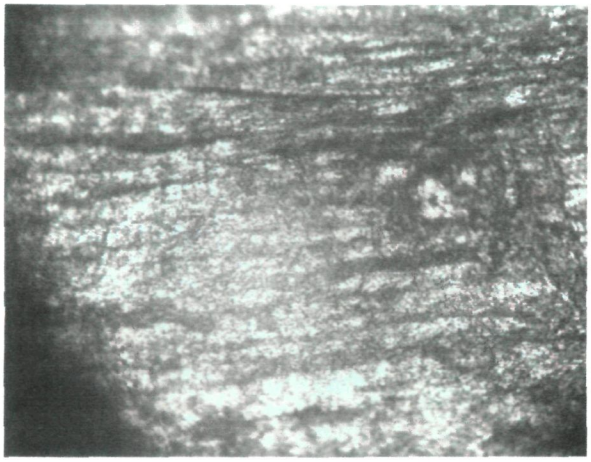
5.8.4 MICROSCOPIC EXAMINATION

The images of the cement slurry coated welded steel wire mesh specimens captured at 400X magnification along with the control and inhibited specimen after 360 *days* of exposure have been shown in Figs. 5.48 – 5.49.

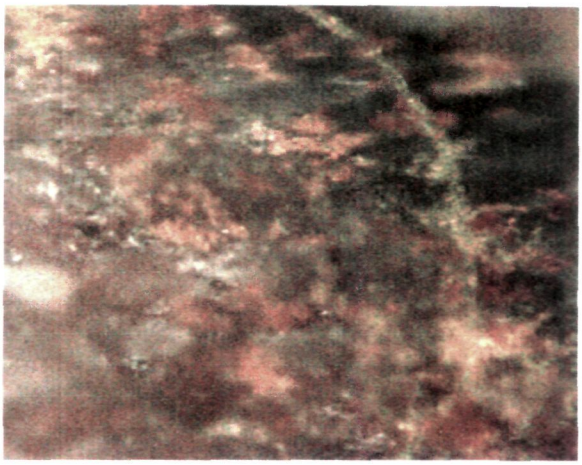
In the Figs. 5.48(a) and 5.49(a), the magnified image of cement slurry coated welded steel wire mesh specimen has been shown which clearly displays the corrosion free surface of the specimen. The cement slurry coated welded steel wire mesh specimen exposed in blank potable water medium after 360 *days* of exposure duration has been shown in Fig. 5.48(b) where high surface corrosion covering complete surface can be witnessed. The specimen inhibited with 1% calcium nitrite has been shown in Fig. 5.48(c) where little corrosion activity in form of some localized spots can be seen. In the Fig. 5.48(d), the cement slurry coated welded steel wire mesh specimen with 5% calcium nitrite has been shown wherein the specimens clearly show no signs of corrosion with the inhibitors completely putting a check on the corrosion activity. For the cement slurry coated welded steel wire mesh specimens, the tannic acid has also been found to be appreciably effective in reducing the onset of corrosion. Only some localized corroded spots are found for 1% and 5% dose of the inhibitor as may be seen in Figs. 5.48(e) and 5.48(f).

The cement slurry coated welded steel wire mesh specimen exposed in blank saline water medium after 360 *days* of exposure duration has been shown in Fig. 5.49(b) where severe corrosion covering full surface has been noticed. The specimen inhibited with 1% calcium nitrite has been shown in Fig. 5.49(c) where mild surface corrosion spread over almost 40–50% of the surface area is observed. In the Fig. 5.49(d), the specimen inhibited with 5% dose of calcium nitrite has been shown where non traceable to a very few isolated spots of corrosion are noticed.

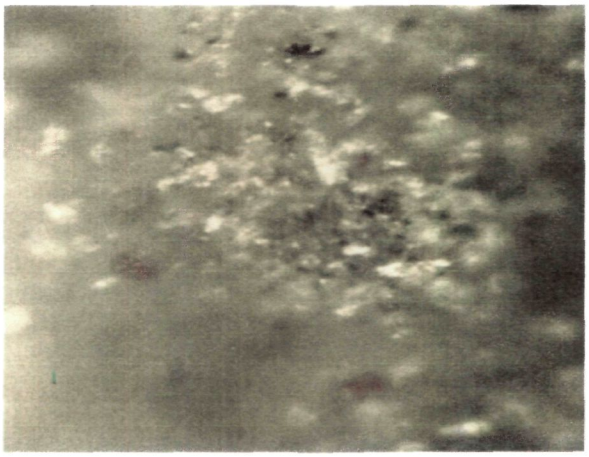
As observed for potable water medium, the tannic acid is also found to be quite effective in controlling/mitigating the onset of corrosion for cement slurry coated welded steel wire mesh specimens. At 1% dose of tannic acid only nominal traces of corrosion are observed in saline water medium as shown in Fig. 5.49 (e). For 5% dose of tannic acid even a better performance in saline water was noticed as shown in Fig. 5.49(f).



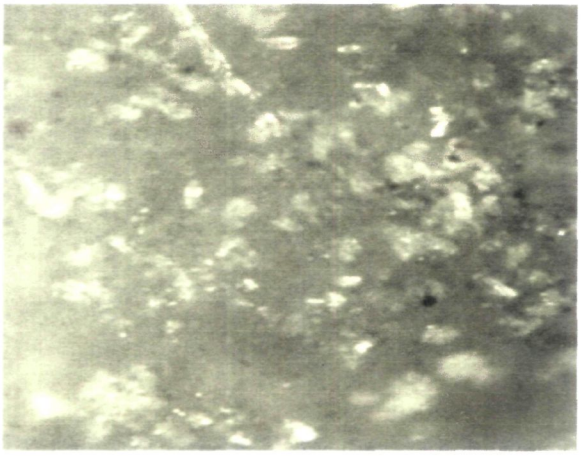
(a) Virgin Wire Mesh Specimen



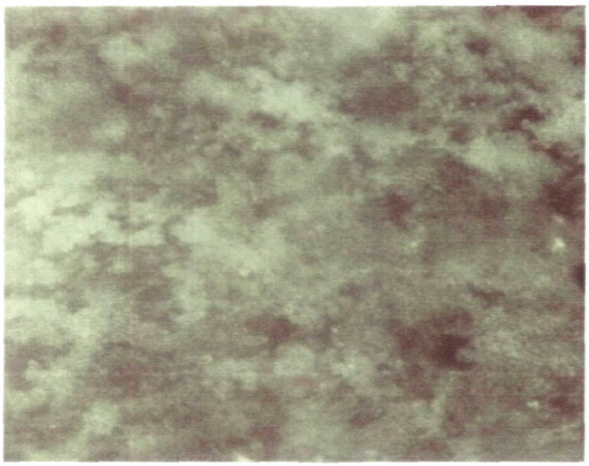
(b) Blank-1 (Potable Water)



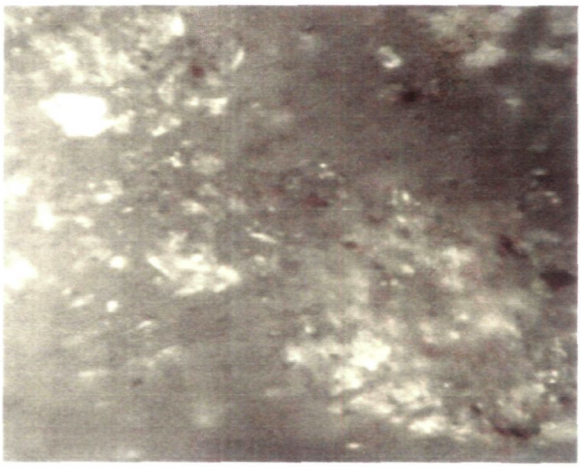
(c) 1% Calcium Nitrite



(d) 5% Calcium Nitrite

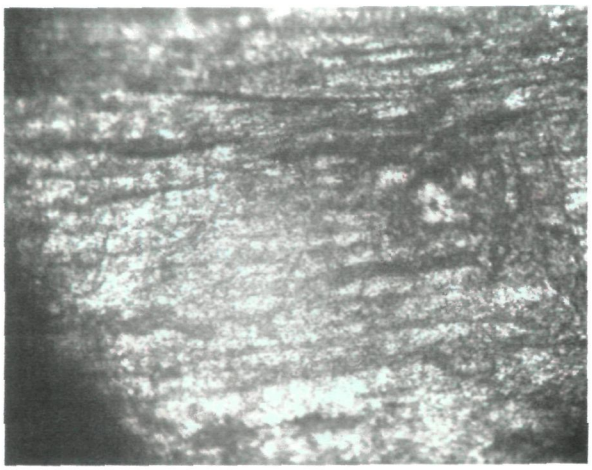


(e) 1% Tannic Acid

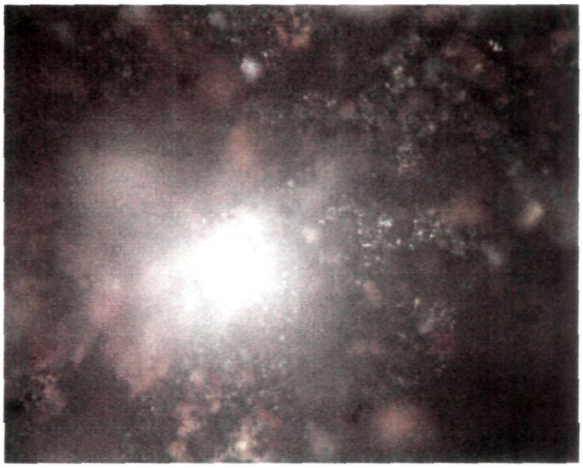


(f) 5% Tannic Acid

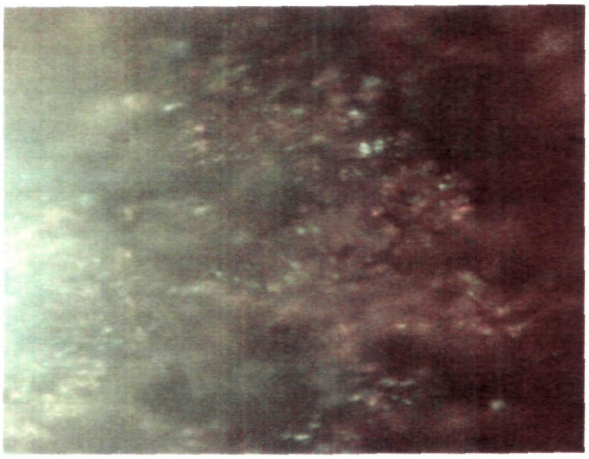
Fig. 5.48 Microscopic Images at 400X Magnification of Cement Slurry Coated Welded Steel Wire Mesh Specimen after 360 *days* of Exposure in Potable Water Medium



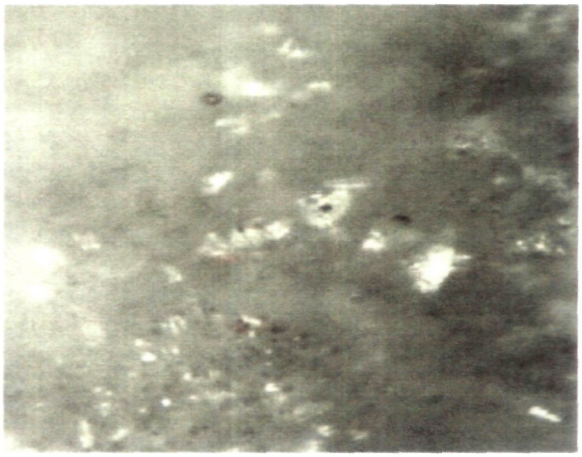
(a) Virgin Wire Mesh Specimen



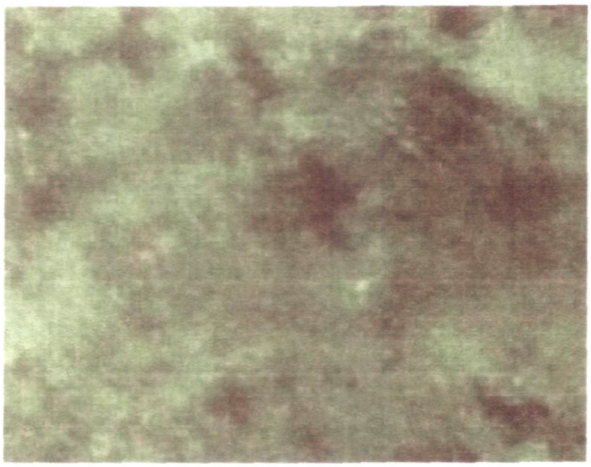
(b) Blank-2 (Saline Water)



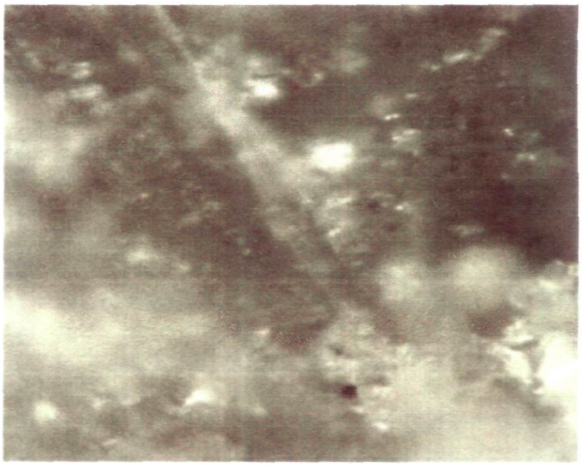
(c) 1% Calcium Nitrite



(d) 5% Calcium Nitrite



(e) 1% Tannic Acid



(f) 5% Tannic Acid

Fig. 5.49 Microscopic Images at 400X Magnification of Cement Slurry Coated Welded Steel Wire Mesh Specimen after 360 *days* of Exposure in Saline Water Medium

A comparison of the images of inhibited specimens with the virgin and control specimen clearly reveals that both calcium nitrite and the tannic acid have been effective in mitigating corrosion. Calcium nitrite was only partially able to inhibit corrosion even at 1% concentration in potable water medium; however at 5% dose the specimen was found to be completely free from any trace of corrosion. In saline water medium, a mild corrosion has been observed at 1% concentration of calcium nitrite. At higher dose *i.e.* at 5% concentration of calcium nitrite in saline water, almost corrosion free surface can be viewed. Contrary to the earlier findings for the case of mild steel plate specimen and the welded steel wire mesh specimen, tannic acid is found to impart satisfactory performance for the slurry coated welded steel wire mesh specimens. At 1% concentration of tannic acid, nominal traces of corrosion were observed both in potable and saline water medium. For 5% concentration of tannic acid, even a better performance both in potable and saline water was achieved. These observations are completely in conformity with the observations of the gravimetric weight loss analysis presented earlier.

5.9 CONCLUDING REMARKS

In the present Chapter an attempt has been made to investigate the effectiveness of the two corrosion inhibitors chosen for the second stage of study. The variables selected were types of the specimen, dose of the inhibitors, exposure duration and exposure medium. The parameters investigated were corrosion inhibition efficiency, corrosion rate and penetration rate. Apart from quantitative study, qualitative observations were also made.

For all the three types of specimen *viz.* mild steel plate, naked welded steel wire mesh and the cement slurry coated welded steel wire mesh specimens, it has been observed that the specimens exposed in saline water medium experience higher corrosion than the corresponding specimens exposed in potable water medium throughout the exposure duration.

For the mild steel specimen, it has been observed that only 1% dose of the calcium nitrite is sufficient in controlling the corrosion throughout the exposure duration. In saline water medium, 1% dose is effective only up to short duration of exposure. However, for longer durations in saline water medium, calcium nitrite dose of 3% was found to be sufficient.

In controlling/delaying the corrosion/onset of corrosion tannic acid has not been found to be very effective owing to the dissolution of protective coating in the aqueous solution. This phenomenon has been found to be more profound in saline water medium for longer duration of exposure.

Almost similar findings as that of the mild steel plate specimen were observed for the naked welded steel wire mesh specimens. Here also, 1% dose of the calcium nitrite is found to be sufficient in controlling the specimen throughout the exposure duration in tap water medium. In saline water medium, 1% dose is effective only up to short duration of exposure. For longer durations in saline water medium, calcium nitrite dose of just above 3% is found to be sufficient as very nominal corrosion is observed only at one of the edge of the specimen exposed in solution inhibited with 3% dose of calcium nitrite. However, at 5% dose the specimen was almost in fully passive state. In controlling the corrosion tannic acid has not been found so effective mainly in saline water medium for longer duration of exposure. The reason may again be attributed to the ineffectiveness of the protective coating of tannic acid in preventing corrosion.

For the cement slurry coated welded steel wire mesh specimens the calcium nitrite dose of 3% has been found to sufficient in checking the corrosion both in potable and saline water medium. For the tannic acid, almost similar level of protection has been observed for all the doses at all the four stages of exposure duration. Hence, even 1% dose is found to impart satisfactory performance. Probably the cement slurry coat protects the tannic acid film which ultimately helps in corrosion prevention.

The reason behind 1% dose of calcium nitrite being not so effective in saline water medium appears to be the higher chloride to nitrite ratio. Similar observations have been made by Claude *et al.* (1998) and Pyc (1999). They concluded that calcium nitrite is ineffective when the chloride to nitrite ratio exceeds approximately 1.0. The reason behind tannic acid not being so effective in mitigating the corrosion process is perhaps the protective coating formed on metal surface that gets dissolved in aqueous solution with the passage of time. Similar observations have been reported in literature by a few other investigators also (Morcillo, *et al.* 1992; Matamala, Smeltzer and Droguett, 1994; Al-Mayouf, 1997).

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[2] **ASTM G1-03** (2003) – Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, ASTM International, U.S.A.

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Chapter 6

Tests on Ferrocement Cuboids

6.1 GENERAL

In the preceding chapters investigations aimed at exploring the effectiveness vis-à-vis selections of appropriate corrosion inhibitors for composites were undertaken. In the present chapter an attempt has been made to explore the worthiness of corrosion inhibitors in controlling/mitigating corrosion in a real ferrocement environment. The investigations were carried out on ferrocement cuboid specimens in which three layers of welded wire meshes were impregnated with rich cement sand mortar. As a matter of fact, the effectiveness of these corrosion inhibitors under direct exposure condition has already been established in the preceding chapters. However, to arrive at a definite conclusion regarding the effectiveness of the inhibitors as well as their role in enhancing the durability of reinforced composites; and hence the useful service life of the structure made up of these composites, it is essential to conduct investigations by exposing these inhibited composite specimens to varying levels of severity. The investigation scheme comprised of two already chosen inhibitors *viz.* calcium nitrite (Type-I) and tannic acid (Type-II). The ferrocement cuboids specimens were exposed to simulated environment over a period of 360 *days*. Apart from visual observations gravimetric weight loss method was also used for quantifying the amount of corrosion. The details of the specimen and the experimental programme are given below.

6.2 EXPERIMENTAL DETAILS

Ferrocement cuboid specimens were cast with the wire meshes embedded inside it, in three layers. The details of the welded wire mesh which was used throughout this part of the study have been given in Table– 6.1. The corrosion inhibitors were used in different ways with the sole objective of finding out the most effective and efficient application methodology.

The Type-I inhibitor *i.e.* calcium nitrite in the first application mode was mixed directly into the cement sand mix by weight of the cement. In the second case it was mixed in cement slurry by weight of cement and the resulting paste was used to form a coating of this inhibited cement slurry over the surface of the wire mesh. The Type-II inhibitor *i.e.* tannic acid was also used in two ways. In the first case, coating of tannic acid was directly formed as a thin film over the wire mesh as explained in the Section- 5.3. The second mode of application of tannic acid was such that a protective coating of plain cement slurry was applied over the film of tannic acid. Each category of the wire meshes were used to cast ferrocement cuboids in triplicate. These four types of specimens with varying dose of inhibitors taken as 1%, 3% and 5%, were exposed to alternate wetting and drying cycles under both potable and saline water (4% *NaCl*) for a duration of 30, 90, 180 and 360 *days*. Each cycle comprised of 5 *days* wet and 5 *days* dry duration. The details of investigation scheme are given in Table– 6.2.

Table– 6.1 Detail of the Welded Wire Mesh Specimens Used for Ferrocement Cuboids

Parameters	**Dimensions**
Size of the Specimen	32×32 *mm*
Diameter	1.42 *mm*
Opening Size	16 *mm*

6.3 CASTING OF THE FERROCEMENT CUBOID SPECIMENS

Ferrocement cuboid specimens of overall size 38×38×24 *mm* were cast with the wire meshes in three layers embedded in the mortar matrix with a minimum cover of 6 *mm* available to the exterior wire meshes. The mould used for the casting of the cuboids is shown in Fig. 6.1. It comprises of four flats on each side mounted over a base plate with the help of nuts and bolts. The thickness of each flat is 6 *mm*. Initially, top three layers of flats were removed and only one flat, each on all four sides was held in position. The mortar was placed inside the mould such that a mortar layer of 6 *mm* was obtained. On this mortar layer, a piece of pre-weighed wire mesh was put. Afterwards, the other set of four flats, one each at all four sides, was put in position and the layer of mortar was put. The second layer of pre-weighed wire mesh was then laid on the mortar layer.

This process was repeated until a thickness of 24 *mm* was achieved. Some of the cast ferrocement cuboid specimens are shown in Fig. 6.2. The ferrocement cuboid specimens under wetting and drying cycles are shown in Fig. 6.3 and Fig. 6.4, respectively.

Table– 6.2 Investigation Scheme for Ferrocement Cuboids

Exposure Mediums (Systems of Exposure)	**Dose of Inhibitor (%)**	**Designation of Exposure Medium**	**Duration of Exposure (*days*)**
Potable Water (Blank-1)	0	NW	30, 90, 180 and 360
Potable Water with Inhibitor Type-I (Calcium Nitrite Mixed in Mortar)	1	NW I-1	30, 90, 180 and 360
	3	NW I-3	30, 90, 180 and 360
	5	NW I-5	30, 90, 180 and 360
Potable Water with Inhibitor Type-I (Calcium Nitrite in Slurry Coated Form)	1	NW SC I-1	30, 90, 180 and 360
	3	NW SC I-3	30, 90, 180 and 360
	5	NW SC I-5	30, 90, 180 and 360
Potable Water with Inhibitor Type-II (Tannic Acid Coating)	1	NW II-1	30, 90, 180 and 360
	3	NW II-3	30, 90, 180 and 360
	5	NW II-5	30, 90, 180 and 360
Potable Water with Inhibitor Type-II (Tannic Acid Coating Protected with Cement Slurry)	1	NW SC II-1	30, 90, 180 and 360
	3	NW SC II-3	30, 90, 180 and 360
	5	NW SC II-5	30, 90, 180 and 360
Saline Water (Blank-2)	0	SW	30, 90, 180 and 360
Saline Water with Inhibitor Type-I (Calcium Nitrite Mixed in Mortar)	1	SW I-1	30, 90, 180 and 360
	3	SW I-3	30, 90, 180 and 360
	5	SW I-5	30, 90, 180 and 360
Saline Water with Inhibitor Type-I (Calcium Nitrite in Slurry Coated Form)	1	SW SC I-1	30, 90, 180 and 360
	3	SW SC I-3	30, 90, 180 and 360
	5	SW SC I-5	30, 90, 180 and 360
Saline Water with Inhibitor Type-II(Tannic Acid Coating)	1	SW II-1	30, 90, 180 and 360
	3	SW II-3	30, 90, 180 and 360
	5	SW II-5	30, 90, 180 and 360
Saline Water with Inhibitor Type-II (Tannic Acid Coating Protected with Cement Slurry)	1	SW SC II-1	30, 90, 180 and 360
	3	SW SC II-3	30, 90, 180 and 360
	5	SW SC II-5	30, 90, 180 and 360

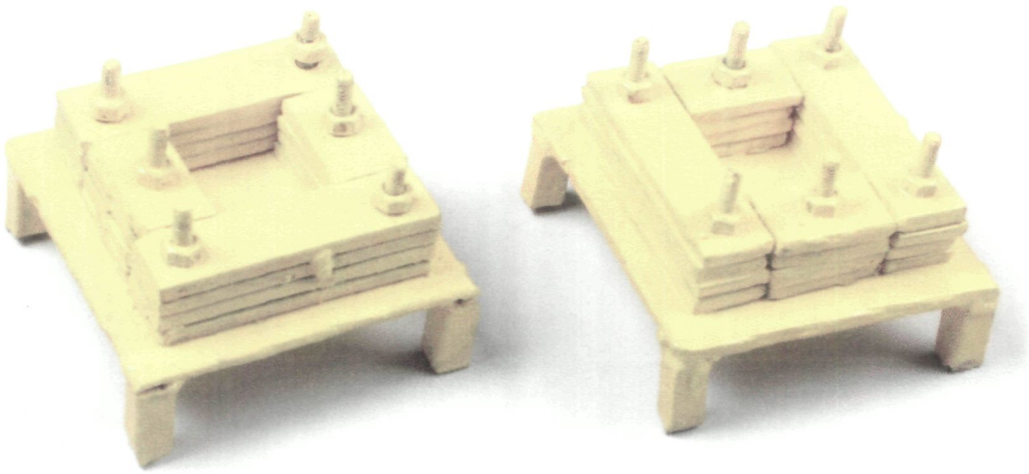

Fig. 6.1 Moulds used for the Ferrocement Cuboids

Fig. 6.2 Ferrocement Cuboids

Fig. 6.3 Ferrocement Cuboids undergoing Wet Cycle

Fig. 6.4 Ferrocement Cuboids undergoing Dry Cycle

6.4 TESTING OF THE FERROCEMENT CUBOID SPECIMENS

The ferrocement cuboid specimens were exposed to wetting and drying cycles of 5 *days* duration each. The wire meshes were taken out by breaking and splitting the ferrocement cuboid specimens after 30, 90, 180 and 360 *days* of exposure that is after 3, 9, 18 and 36 wetting and drying cycles. These wire meshes were cleaned as per the recommendations of ASTM G1– 03 Annexure–A1, dried and re-weighed so that weight loss if any can be obtained. Gravimetric weight loss study was carried out and the corrosion inhibition efficiency, corrosion rate and penetration rate were obtained using Eqns. 5.1-5.3.

6.5 EVALUATION OF CORROSION IN OUTER WIRE MESH LAYER

The outer wire meshes were taken out from the ferrocement cuboids, soon after the specified exposure duration as mentioned in Table– 6.2. These meshes were then cleaned and the loss of weight was recorded. Using the observed weight loss, corrosion inhibition efficiency, corrosion rate and penetration rate were calculated as explained in the Chapter–5. The results are given in Tables– 6.3 to 6.6 and also shown in Figs. 6.5 – 6.22. The tested welded steel wire mesh specimens after 360 *days* of exposure under different mediums are shown in Figs. 6.23 – 6.30.

6.5.1 EFFECT OF INHIBITOR DOSE

The dose of the inhibitors was varied as 1%, 3% and 5% for both calcium nitrite and tannic acid. The effect of the variation of the dose of corrosion inhibitors on corrosion inhibition efficiency, corrosion rate and penetration rate has been discussed in the following sub-sections.

6.5.1.1 CORROSION INHIBITION EFFICIENCY

The corrosion inhibition efficiency exhibited by the calcium nitrite and tannic acid for the cuboid specimens is given in Tables– 6.3–6.4 and shown in Figs. 6.5 – 6.8. The corrosion inhibition efficiency has been found to increase with the increase in the dose of the inhibitors except in the potable water medium at 30 *days* apparently because of negligible corrosion activity resulting in equally negligible weight loss in control as well as the inhibited specimens after 30 *days* of exposure. Almost similar observations were made in the visual inspection where the corrosion initiation was un-traceable both in control and inhibited specimens.

For the cuboid specimens cast with calcium nitrite inhibited mortar and exposed in potable water (NW I), it has been observed that the corrosion inhibition efficiency increases substantially as the dose of the calcium nitrite is increased from 1% to 3%, however, with further increase in the dose to 5%, only a marginal increase in the efficiency is observed. In saline water condition (SW I), almost similar trends were observed, except at the 30 *days*, where even for the 1% dose of calcium nitrite, the corrosion inhibition efficiency above 71% and 82% has been observed in potable and saline water medium respectively for all other exposure duration. For 5% dose of the inhibitor, the efficiency has been observed to be as high as 95% in potable water exposure medium and above 97% in saline water exposure medium.

For the cuboids specimens cast with wire meshes coated with the calcium nitrite inhibited cement slurry and exposed in potable and saline water medium (NW SC I and SW SC I), very high efficiency was observed except for the potable water exposure medium at 30 *days*, the reason behind this lower efficiency is apparently the negligible corrosion activity encountered for this time duration. At 1% dose of calcium nitrite, efficiency above 91% in potable water and above 83% in saline water exposure medium has been observed. As the dose is increased to 5%, the efficiency reaches above 97%, both in potable and saline water exposure medium.

Table-6.3 Average Weight Loss and Corrosion Inhibition Efficiency for Outer Layer Wire Mesh of Cuboids Exposed in Potable Water

S. No.	Systems of Exposure	30 *days*		90 *days*		180 *days*		360 *days*	
		Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)
1.	NW	0.267	---	11.700	---	31.133	---	70.333	---
2.	NW I-1	0.167	37.45	1.816	84.48	8.833	72.27	19.783	71.87
3.	NW I-3	0.150	43.82	0.783	93.31	2.183	92.99	5.900	91.61
4.	NW I-5	0.133	50.19	0.416	96.44	1.350	95.66	3.516	95.00
5.	NW SC I-1	0.150	43.82	0.883	92.88	2.383	92.34	6.061	91.45
6.	NW SC I-3	0.183	31.46	0.367	96.86	1.083	96.53	2.816	96.00
7.	NW SC I-5	0.083	68.91	0.217	98.14	0.633	97.97	1.583	97.75
8.	NW II-1	0.217	5.00	2.316	80.20	8.900	71.41	22.650	67.78
9.	NW II-3	0.100	62.55	2.250	80.77	7.933	74.52	21.416	69.55
10.	NW II-5	0.116	56.55	1.633	86.04	6.233	80.00	18.600	73.55
11.	NW SC II-1	0.133	50.19	1.050	91.02	4.000	87.15	9.916	85.90
12	NW SC II-3	0.233	12.73	0.816	93.02	3.917	87.42	10.183	85.52
13.	NW SC II-5	0.150	43.82	0.800	93.16	3.483	88.81	9.783	86.09

Table- 6.4 Average Weight Loss and Corrosion Inhibition Efficiency for Outer Layer Wire Mesh of Cuboids Exposed in Saline Water

S. No.	Systems of Exposure	30 *days*		90 *days*		180 *days*		360 *days*	
		Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)	Average Weight loss (*mg*)	Efficiency (%)
1.	SW	4.916	---	25.450	---	66.017	---	147.200	---
2.	SW I-1	0.200	95.93	2.483	90.24	10.000	84.85	26.016	82.33
3.	SW I-3	0.116	97.64	1.000	96.07	6.917	89.52	15.167	89.70
4.	SW I-5	0.083	98.31	0.567	97.78	1.683	97.45	3.933	97.33
5.	SW SC I-1	0.233	95.26	2.500	90.18	9.167	86.11	24.050	83.66
6.	SW SC I-3	0.217	95.58	1.883	92.60	7.100	89.24	18.133	87.68
7.	SW SC I-5	0.050	98.98	0.350	98.62	1.483	97.75	4.150	97.18
8.	SW II-1	0.300	93.90	5.083	80.03	14.167	78.54	35.033	76.20
9.	SW II-3	0.183	96.28	3.083	87.88	11.333	82.83	28.100	80.91
10.	SW II-5	0.167	96.60	2.450	90.37	7.567	88.54	22.067	85.00
11.	SW SC II-1	0.200	95.93	3.517	86.18	11.100	83.19	26.100	82.27
12	SW SC II-3	0.250	94.91	2.000	92.14	7.033	89.35	19.183	86.97
13.	SW SC II-5	0.100	97.96	1.900	92.53	6.967	89.45	18.516	87.42

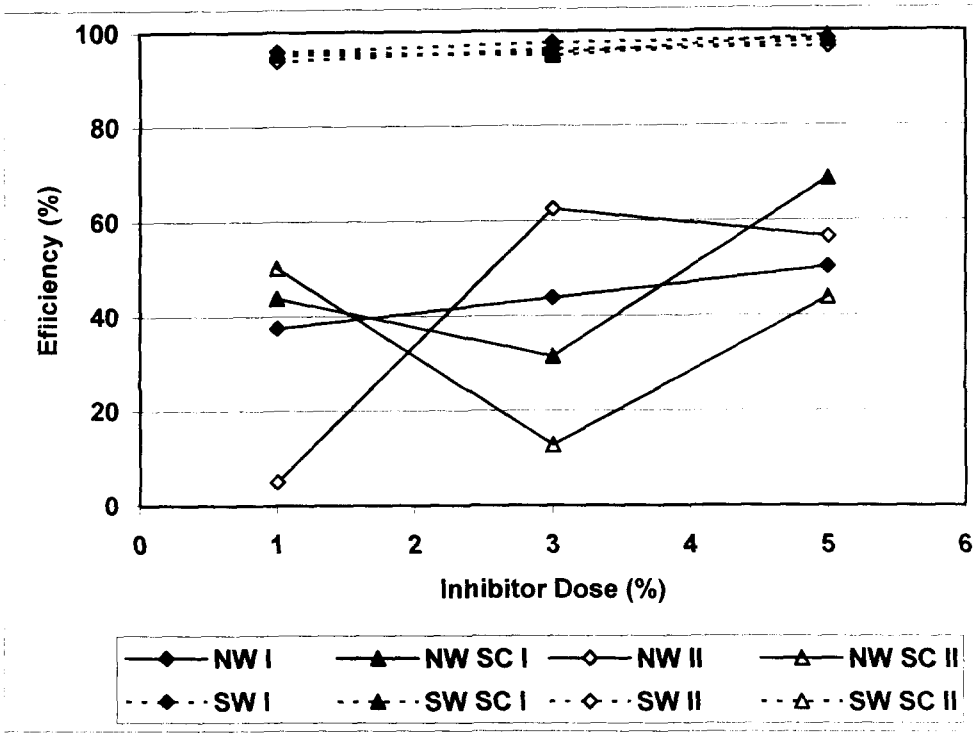

Fig. 6.5 Efficiency of Corrosion Inhibitors for Outer Layer Wire Mesh of Ferrocement Cuboids after 30 *days* of Exposure

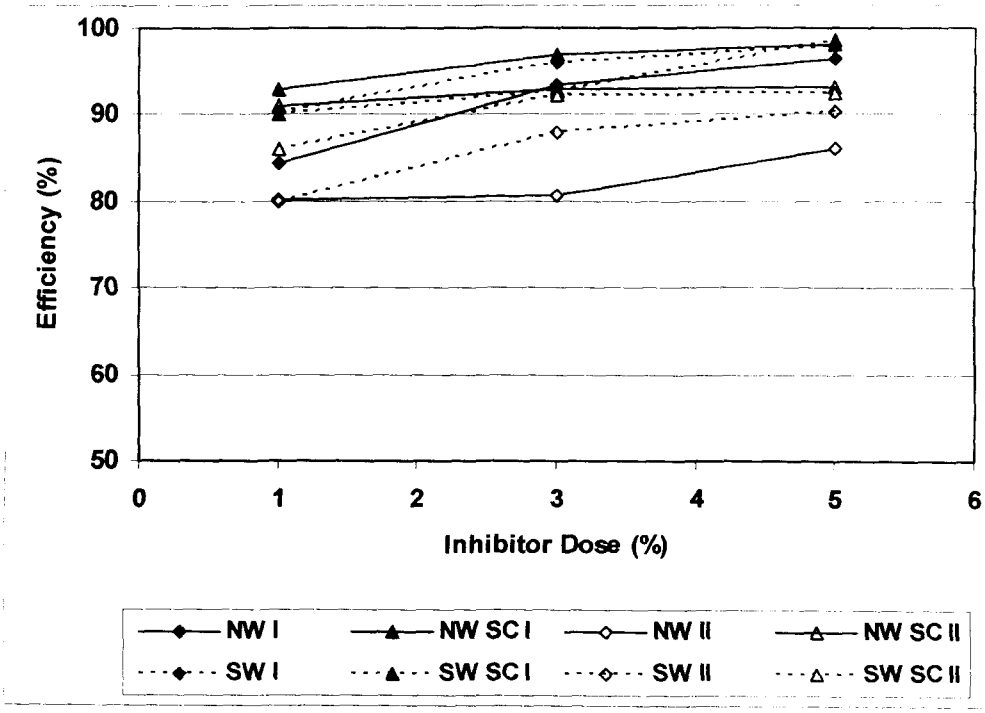

Fig. 6.6 Efficiency of Corrosion Inhibitors for Outer Layer Wire Mesh of Ferrocement Cuboids after 90 *days* of Exposure

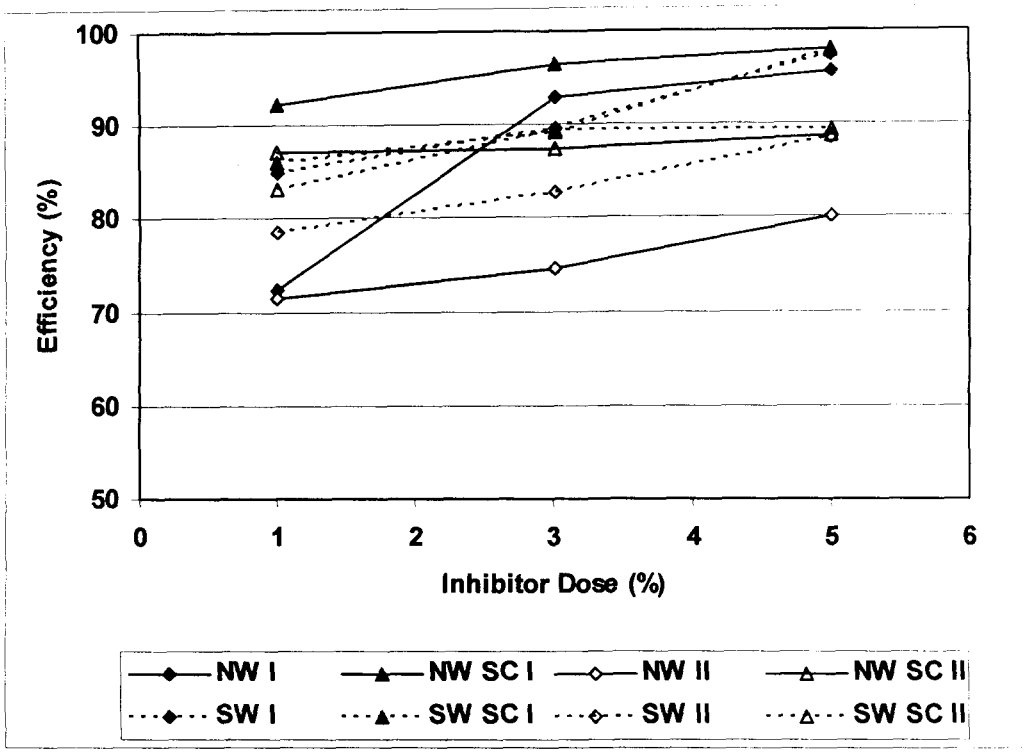

Fig. 6.7 Efficiency of Corrosion Inhibitors for Outer Layer Wire Mesh of Ferrocement Cuboids after 180 *days* of Exposure

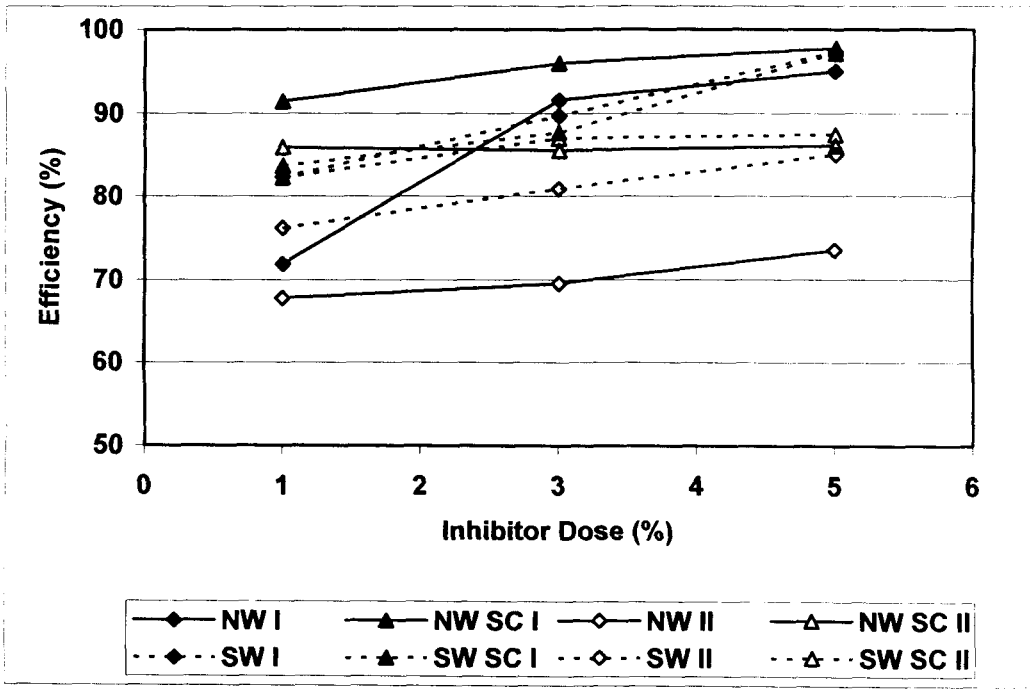

Fig. 6.8 Efficiency of Corrosion Inhibitors for Outer Layer Wire Mesh of Ferrocement Cuboids after 360 *days* of Exposure

For the cuboid specimens cast with the wire mesh having coating of tannic acid (NW II and SW II), the corrosion inhibition efficiency is not that high as observed for calcium nitrite. The efficiency above 67% and 76% has been observed in potable and saline water exposure medium respectively at 1% dose which increases to 77% and 85% at 5% dose. For cuboids cast with the wire mesh having cement slurry coat over tannic film (NW SC II and SW SC II), the efficiency has been found to increase substantially. The efficiency values were found to be 85% in potable water exposure medium and above 82% in saline water exposure medium even for 1% dose. The corresponding values for 5% dose are found to be above 86% in potable and above 87% in saline water medium.

The efficiency for the cuboids having inhibited cement slurry coated wire mesh specimen has been higher as compared to the specimen having calcium nitrite inhibited mortar. The reason behind this may be attributed to the presence of corrosion inhibitor in higher concentration around the wire mesh which eventually forms strong passivating film over the surface of the wire mesh. Despite the fact that due to the ingress of chloride in high concentrations, the depletion of passivating film does take place at such locations, it eventually gets repaired as the inhibitor is still available around the surface of the wire mesh.

6.5.1.2 CORROSION RATE

The corrosion rate observed for the cuboid specimens are given in Table– 6.5 and Table– 6.6 and shown in Figs. 6.9 – 6.12. It has been observed that the corrosion rate in control specimens exposed to saline water is higher than those exposed to potable water. With the increase in the dose of the inhibitors, the corrosion rate is found to decrease.

Extremely low corrosion rate has been observed for both the calcium nitrite inhibited specimens (NW I and NW SC I) exposed in potable water except for the 1% dose (NW I-1), where the corrosion rate is slightly higher but much lower than the control specimen. In specimens inhibited with calcium nitrite and exposed to saline water, medium to very low corrosion rate has been observed for 5% dose. Even for 1% and 3% dose of calcium nitrite, reasonably lower corrosion rate has been observed.

Table- 6.5 Corrosion Rate and Penetration Rate for Outer Layer Wire Mesh of Cuboids Exposed in Potable Water

S. No.	Systems of Exposure	30 *days*		90 *days*		180 *days*		360 *days*	
		Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)
1.	NW	0.026	0.660	0.382	9.703	0.508	12.900	0.574	14.580
2.	NW I-1	0.016	0.406	0.059	1.499	0.144	3.658	0.161	4.089
3.	NW I-3	0.015	0.381	0.026	0.660	0.036	0.914	0.048	1.219
4.	NW I-5	0.013	0.330	0.014	0.356	0.022	0.559	0.029	0.737
5.	NW SC I-1	0.015	0.381	0.029	0.737	0.039	0.991	0.049	1.245
6.	NW SC I-3	0.018	0.457	0.012	0.305	0.018	0.457	0.023	0.584
7.	NW SC I-5	0.008	0.203	0.008	0.203	0.010	0.254	0.013	0.330
8.	NW II-1	0.021	0.533	0.076	1.930	0.145	3.683	0.185	4.699
9.	NW II-3	0.010	0.254	0.073	1.854	0.130	3.302	0.175	4.445
10.	NW II-5	0.011	0.279	0.053	1.346	0.102	2.591	0.152	3.861
11.	NW SC II-1	0.013	0.330	0.034	0.864	0.065	1.651	0.081	2.057
12	NW SC II-3	0.023	0.584	0.027	0.686	0.064	1.626	0.083	2.108
13.	NW SC II-5	0.015	0.381	0.026	0.660	0.057	1.448	0.080	2.032

Table- 6.6 Corrosion Rate and Penetration Rate for Outer Layer Wire Mesh of Cuboids Exposed in Saline Water

S. No.	Systems of Exposure	30 *days*		90 *days*		180 *days*		360 *days*	
		Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)	Corrosion Rate (*mpy*)	Penetration Rate (*μm/yr*)
1.	SW	0.482	12.243	0.831	21.107	1.078	27.381	1.202	30.531
2.	SW I-1	0.020	0.508	0.081	2.057	0.163	4.140	0.212	5.385
3.	SW I-3	0.011	0.279	0.033	0.838	0.113	2.870	0.124	3.150
4.	SW I-5	0.008	0.203	0.018	0.457	0.027	0.686	0.032	0.813
5.	SW SC I-1	0.023	0.584	0.082	2.083	0.150	3.810	0.196	4.978
6.	SW SC I-3	0.021	0.533	0.061	1.549	0.116	2.946	0.148	3.760
7.	SW SC I-5	0.005	0.127	0.011	0.279	0.024	0.610	0.034	0.864
8.	SW II-1	0.030	0.762	0.166	4.216	0.231	5.867	0.286	7.264
9.	SW II-3	0.018	0.457	0.101	2.565	0.185	4.699	0.229	5.817
10.	SW II-5	0.016	0.406	2.032	2.032	0.124	3.150	0.180	4.572
11.	SW SC II-1	0.020	0.508	0.115	2.921	0.181	4.597	0.213	5.410
12.	SW SC II-3	0.024	0.610	0.065	1.651	0.115	2.921	0.157	3.988
13.	SW SC II-5	0.010	0.254	0.062	1.575	0.114	2.896	0.151	3.835

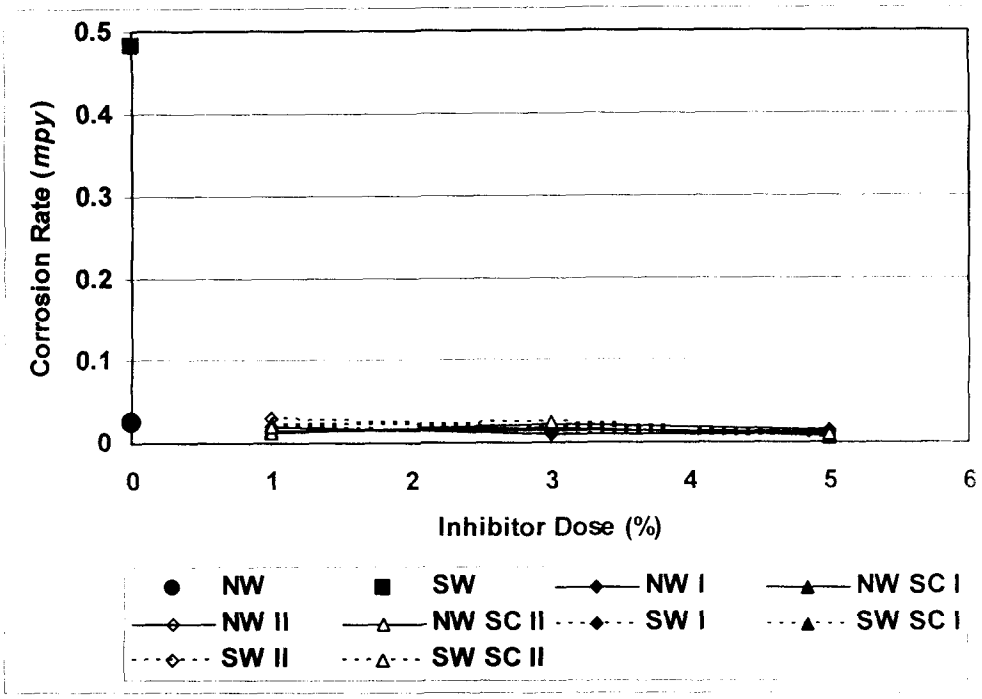

Fig. 6.9 Corrosion Rate for Outer Layer Wire Mesh of Ferrocement Cuboids after 30 *days* of Exposure

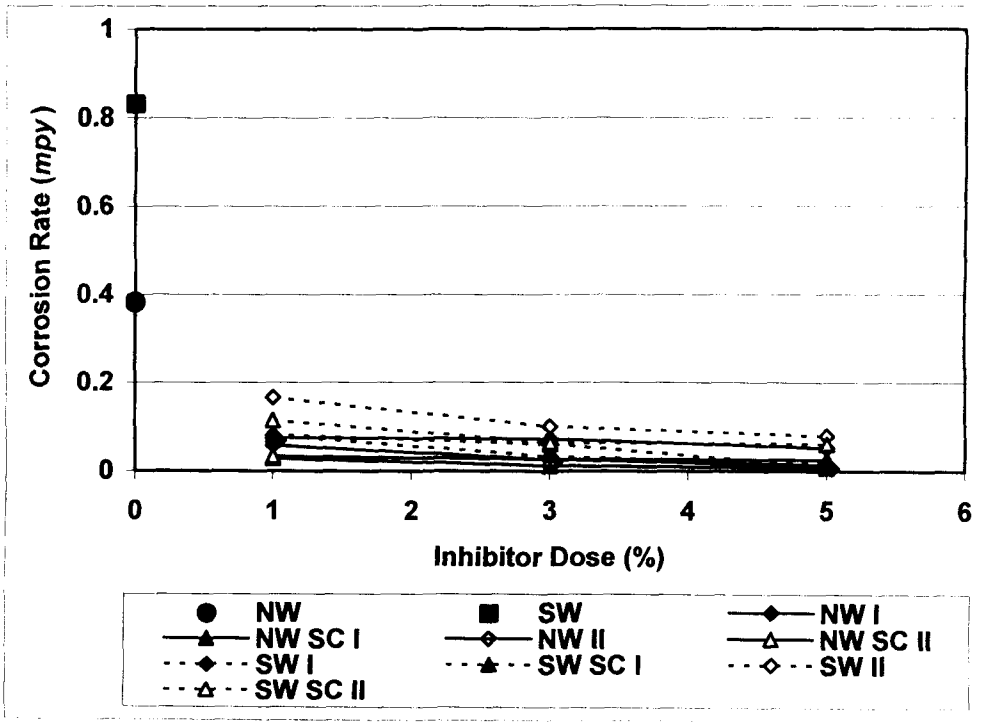

Fig. 6.10 Corrosion Rate for Outer Layer Wire Mesh of Ferrocement Cuboids after 90 *days* of Exposure

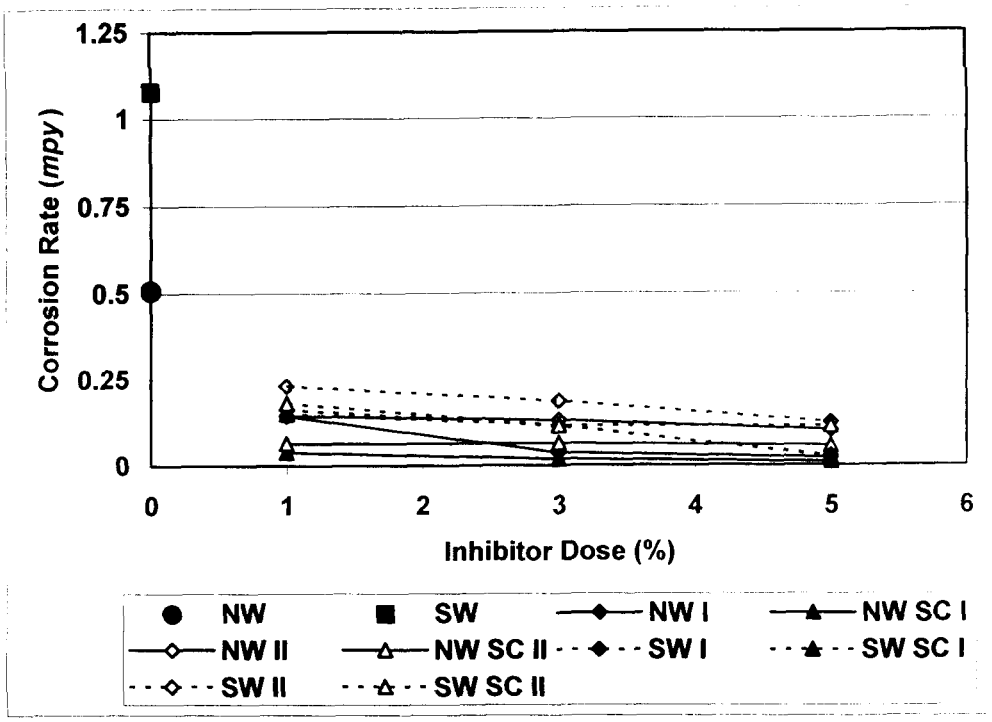

Fig. 6.11 Corrosion Rate for Outer Layer Wire Mesh of Ferrocement Cuboids after 180 *days* of Exposure

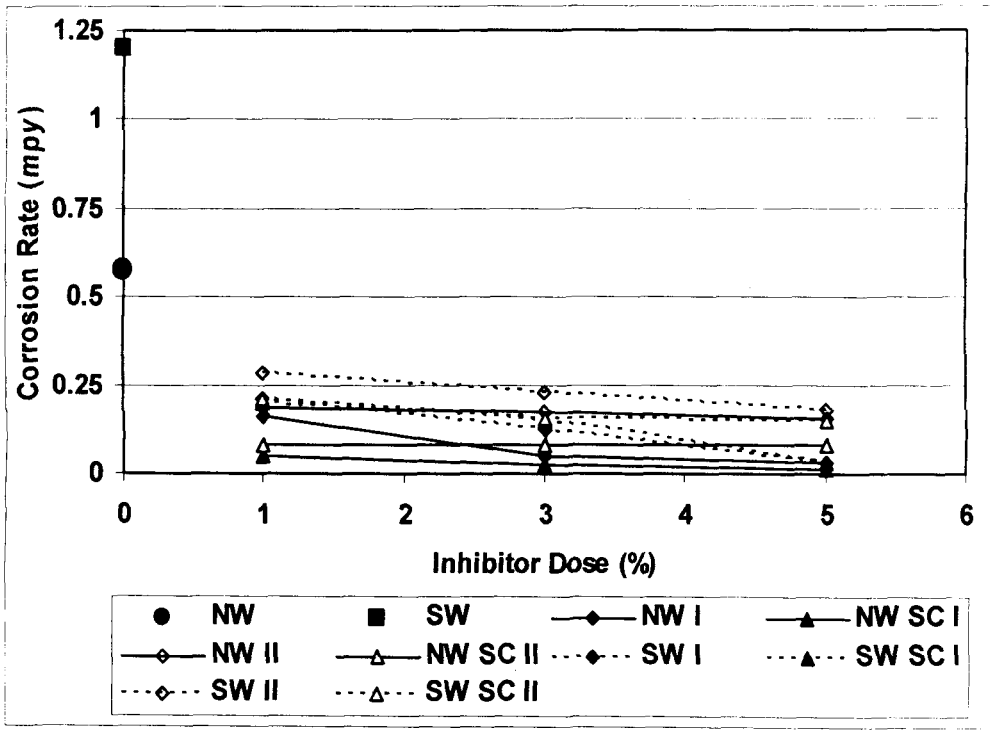

Fig. 6.12 Corrosion Rate for Outer Layer Wire Mesh of Ferrocement Cuboids after 360 *days* of Exposure

Although the tannic acid inhibited specimens exhibited a little higher corrosion rate as compared to calcium nitrite inhibited specimens, still the induced corrosion is observed to be much lower than the respective control specimens and also within the acceptable limits. Among the two ways of application of tannic acid, the cuboids cast with the wire mesh having cement slurry coat over tannic film (NW SC II and SW SC II) have shown better results. For such specimens, very low corrosion rate in potable water medium and reasonably acceptable corrosion rate in saline water medium has been observed. However, the dose of the tannic acid seems to have little influence especially in potable water medium mainly because of the protection provided by the cement slurry coating to the tannic acid film. The film of tannic acid, being well protected by the cement slurry coating, does not dissolve and therefore, remains effective in mitigating corrosion.

6.5.1.3 PENETRATION RATE

The penetration rate has been presented in Table– 6.5 and Table– 6.6 and shown in Figs. 6.13 – 6.16. The value of penetration rate, up to 1–2 *μm/yr* is considered to be very low to passive and the value from 2–6 *μm/yr* is regarded as low to moderate (Law *et al.*, 2003). The values of penetration rate impart extremely satisfactory results for both the specimens inhibited with calcium nitrite (NW I and NW SC I). Especially for the cuboids cast with the inhibited cement slurry coated wire mesh specimen (NW SC I), perfect passive state has been observed even for the 1% dose of the inhibitor as the maximum value of penetration rate has been 1.245 *μm/yr*. For the cuboid specimens cast with calcium nitrite inhibited mortar and exposed in potable water (NW I), the results are well below 2 *μm/yr* for 3% and 5% dose. For 1% dose of calcium nitrite mixed with the mortar, the value of penetration rate has been observed to be 4.089 *μm/yr*, after 360 *days* of exposure, which is below 6 *μm/yr* and hence well within acceptable limits.

For the tannic acid inhibited cuboid specimens, the values are not that low as that of the calcium nitrite inhibited specimens. However, acceptable inhibition has been shown by tannic acid too. In case of cuboids specimen cast with the wire mesh having coating of tannic acid (NW II), the values lie in the range of 2–6 *μm/yr*, after 360 *days* of exposure, which falls in a low to moderate corrosion category.

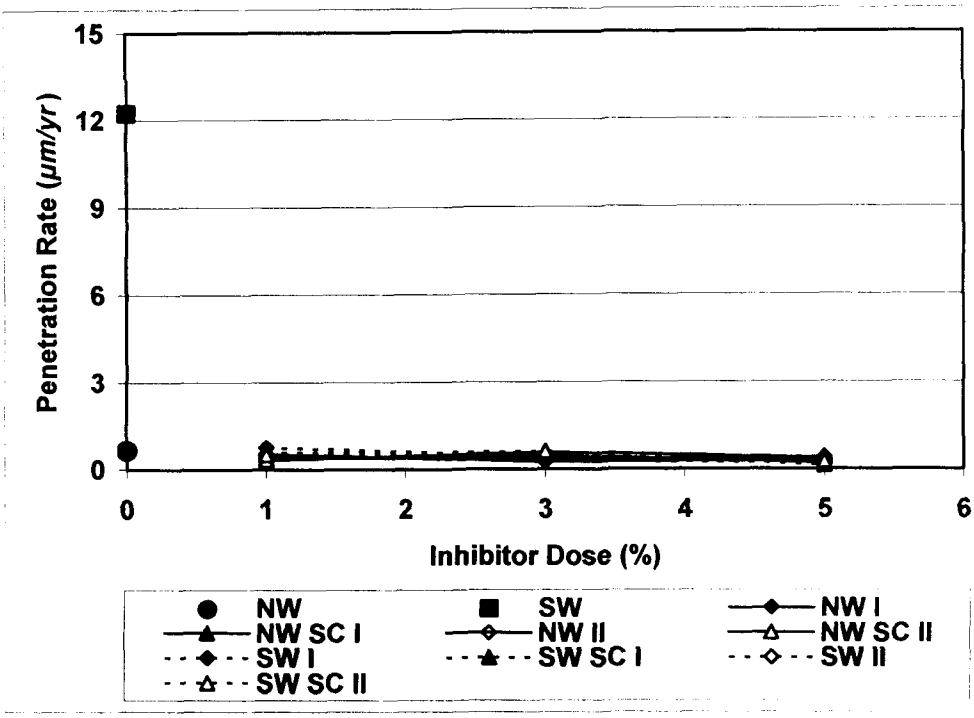

Fig. 6.13 Penetration Rate for Outer Layer Wire Mesh of Ferrocement Cuboids after 30 *days* of Exposure

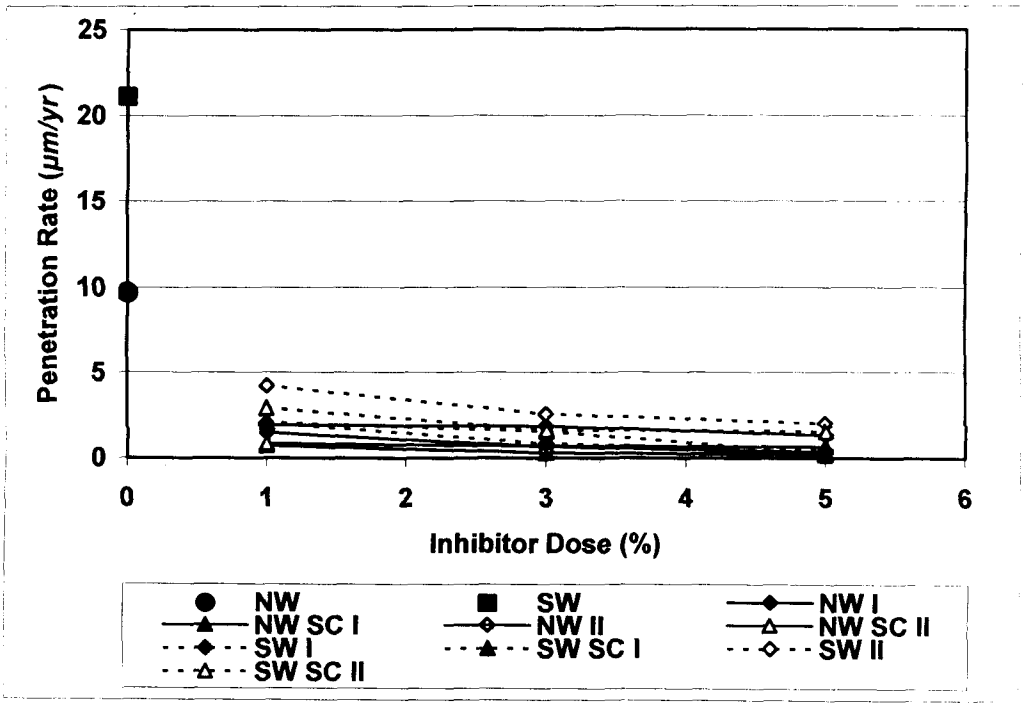

Fig. 6.14 Penetration Rate for Outer Layer Wire Mesh of Ferrocement Cuboids after 90 *days* of Exposure

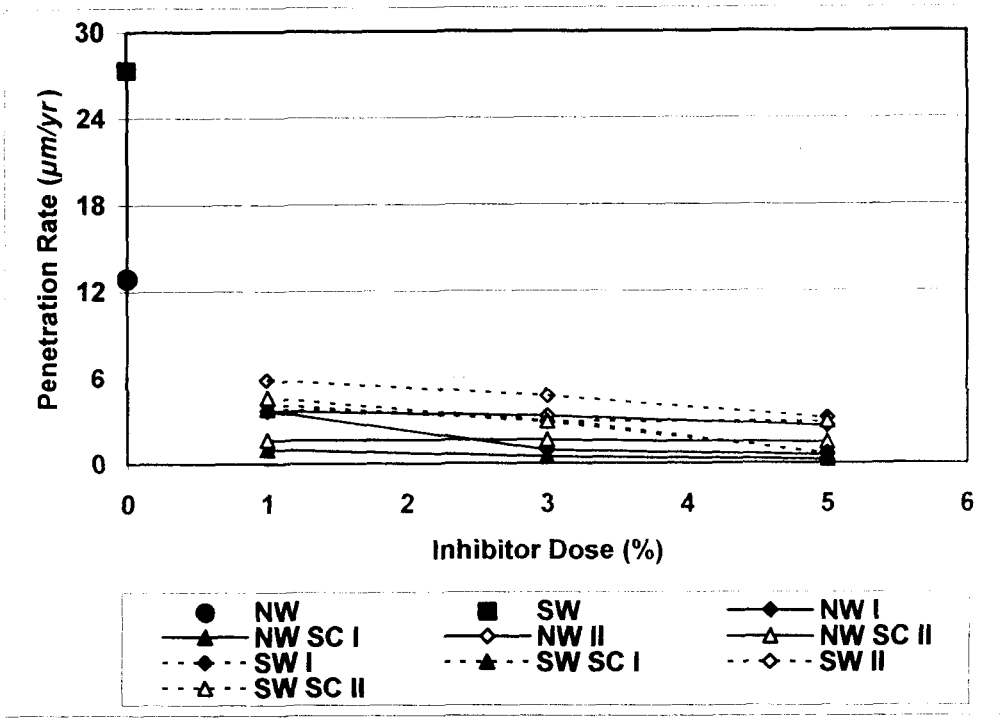

Fig. 6.15 Penetration Rate for Outer Layer Wire Mesh of Ferrocement Cuboids after 180 *days* of Exposure

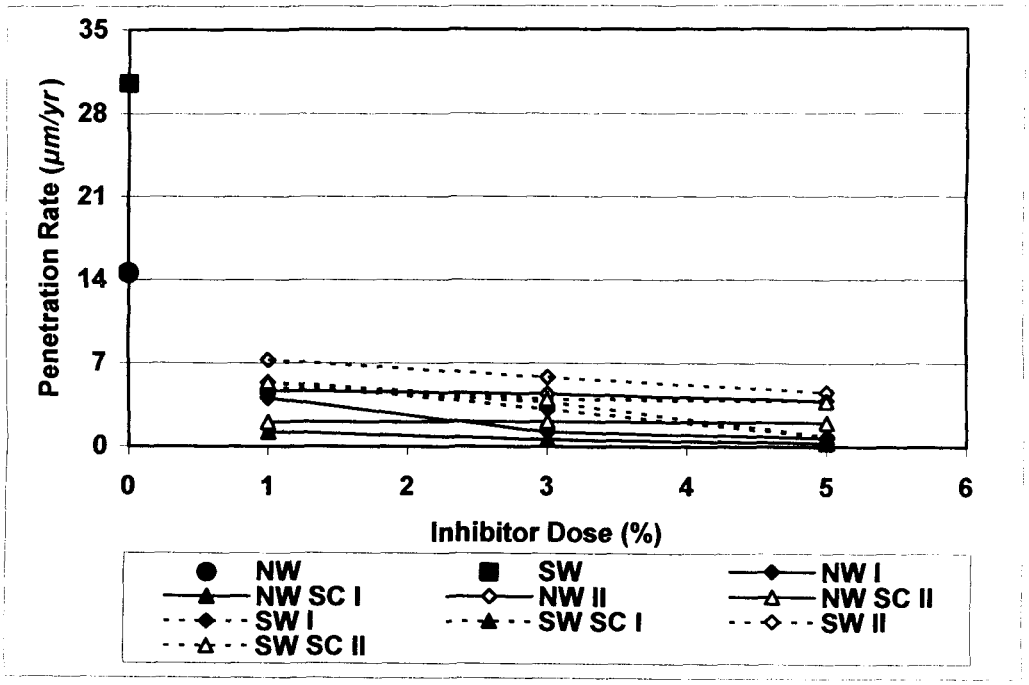

Fig. 6.16 Penetration Rate for Outer Layer Wire Mesh of Ferrocement Cuboids after 360 *days* of Exposure

The results obtained for the second type of specimen inhibited with the tannic acid (NW SC II), penetration rate very near to 2 *μm/yr* has been observed which is far superior than the specimens having no cement slurry protection over coating of the tannic acid over the wire meshes in the normal water medium.

In the saline water medium, calcium nitrite inhibited specimens have shown extremely passive state for only 5% dose, however for 3% dose too, a reasonably high inhibition has been observed. For 1% dose, although the penetration rate values are little on the higher side, but still fall in the range of 2–6 *μm/yr* even after 360 *days* of exposure. For the tannic acid inhibited cuboid specimens, reasonably high inhibition has been observed for the specimens cast with the wire mesh having cement slurry coat over tannic film at 3% and 5% dose. Except for the 1% dose of tannic acid (SW II), all other combinations have penetration rate indicating a mild to moderate corrosion.

6.5.2 EFFECT OF EXPOSURE DURATION

The effect of the exposure duration on corrosion inhibition efficiency, corrosion rate and penetration has been presented in the following sub-sections. The specimens were exposed for 30, 90, 180 and 360 *days*.

6.5.2.1 CORROSION INHIBITION EFFICIENCY

The variation in corrosion inhibition efficiency with exposure duration has been presented in Table– 6.3 and Table– 6.4 and shown in Figs. 6.17 – 6.18. The corrosion activity in the first 30 *days* being almost negligible, the corrosion inhibition efficiency value is observed to be very low on account of mathematical ambiguity. However, the efficiency values indicate a sharp rise between 30 *days* to 90 *days* of exposure. With further increase in the exposure duration above 90 *days*, a marginal reduction in corrosion inhibition efficiency has been observed in most of the combinations. Very high corrosion inhibition efficiency is observed for both the combinations of calcium nitrite (NW I and NW SC I) in potable as well as in saline water medium throughout the period of exposure. The value of corrosion inhibition efficiency in potable water remains more than 91% in majority of the specimen groups except for the 1% dose of the calcium nitrite (NW I), where it reduces to 71% for longer duration of exposure.

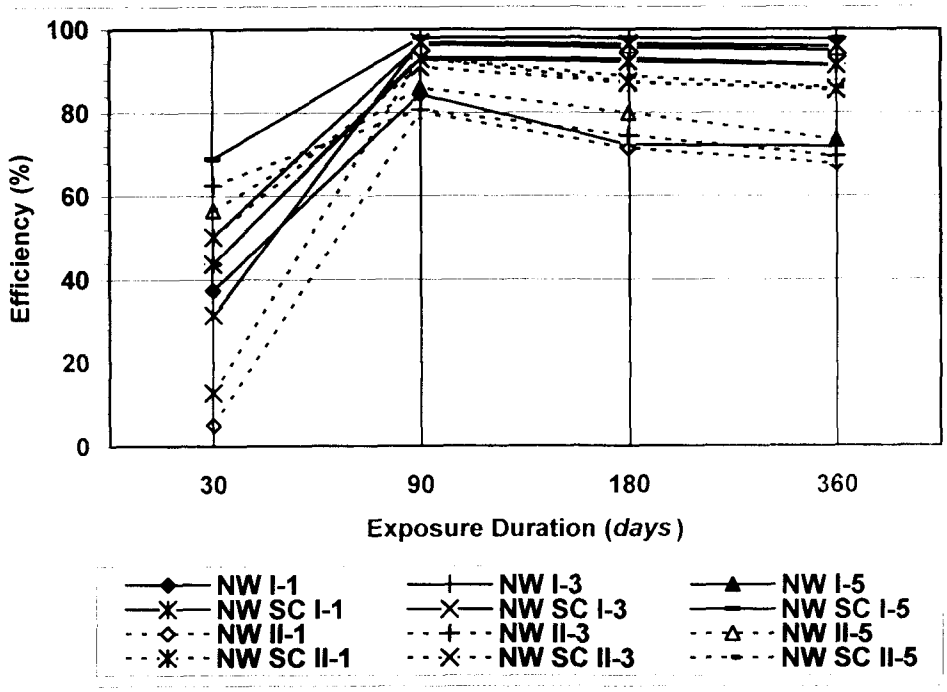

Fig. 6.17 Efficiency of Corrosion Inhibitors for Outer Layer Wire Mesh of Ferrocement Cuboids in Potable Water Medium

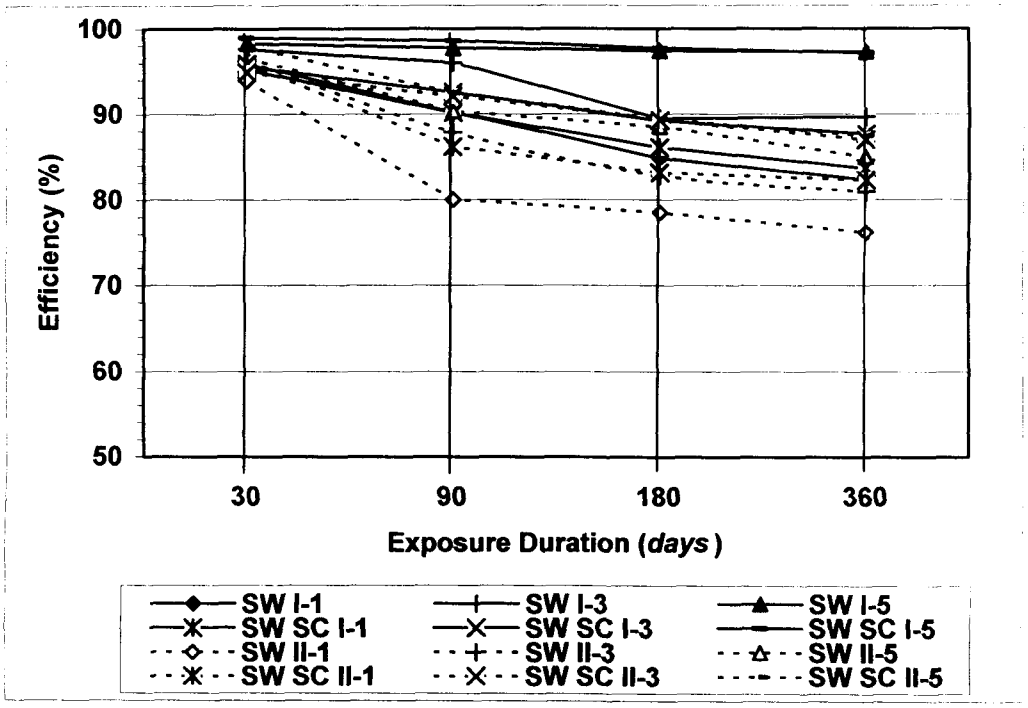

Fig. 6.18 Efficiency of Corrosion Inhibitors for Outer Layer Wire Mesh of Ferrocement Cuboids in Saline Water Medium

For the calcium nitrite inhibited cement slurry coated specimens (NW SC I-5), the efficiency goes up to 97%. In saline water condition, the inhibition efficiency ranges from 82% to 97% for calcium nitrite inhibited specimens (SW SC I).

In case of tannic acid inhibited specimens exposed to potable water (NW II), the corrosion inhibition efficiency is found to vary from 67% to 77% and for the specimen exposed in saline water (SW II), the efficiency has been found to be ranging between 76% – 85%. For the cement slurry coated tannic acid specimen (NW SC II) exposed in potable water, only a marginal variation in the efficiency has been observed with the increase in exposure duration as the values are found to range between 85% – 86%. For the specimens exposed in saline water (SW SC II), the corresponding values are found to be lying in the range of 82% – 87%.

6.5.2.2 CORROSION RATE

The variation of corrosion rate with exposure duration has been presented in Table– 6.3 and Table– 6.4 and shown in Figs. 6.19 – 6.20. Very high corrosion rate has been observed in case of uninhibited specimens exposed to saline water medium (Blank-2), as compared to potable water medium (Blank-1) as well as all the other corrosion inhibited specimen groups. This observation holds for all the four stages of exposure durations *i.e.* 30, 90, 180 and 360 *days*.

In potable water exposure medium, except for the 1% dose of the calcium nitrite, where the corrosion rate is high for the longer duration of the exposure, exceptionally low corrosion rate has been observed for all other specimens inhibited with calcium nitrite. For the tannic acid inhibited specimens in whom the tannic acid film has been protected by the cement slurry coating (NW SC II), extremely low corrosion rate has been exhibited. However, for the other tannic acid inhibited specimen (NW II) the corrosion rate is comparatively higher but much lower than the control specimens (Blank-1).

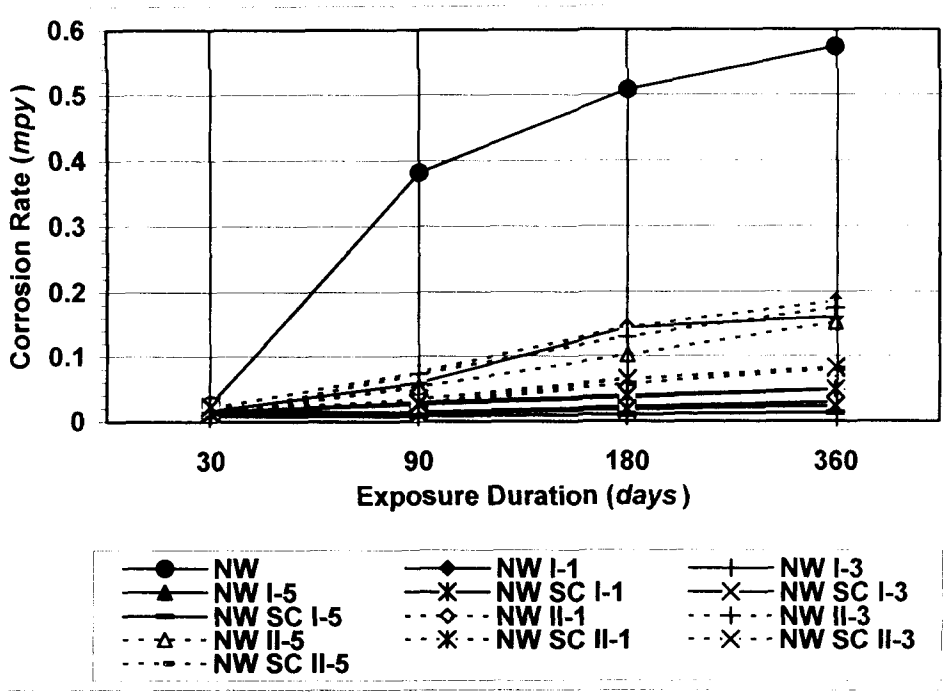

Fig. 6.19 Corrosion Rate for Outer Layer Wire Mesh of Ferrocement Cuboids in Potable Water Medium

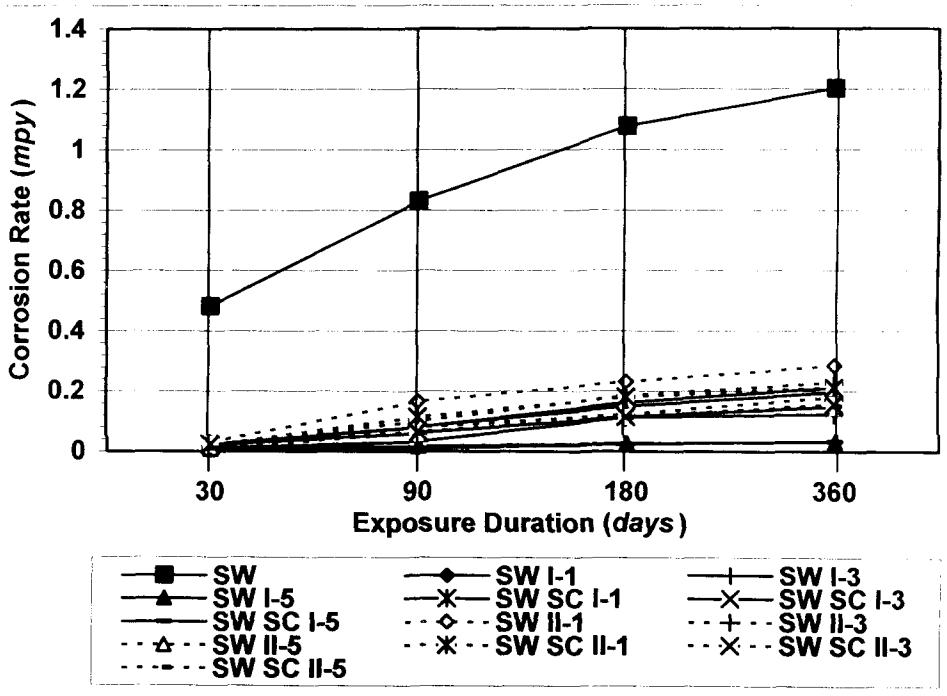

Fig. 6.20 Corrosion Rate for Outer Layer Wire Mesh of Ferrocement Cuboids in Saline Water Medium

In saline water exposure medium, the calcium nitrite inhibited specimens, having inhibited mortar (SW I-5) as well as those coated with the inhibited cement slurry (SW SC I-5), performed very well. For other combinations, the corrosion rate is not that low but still remains much lower than the control specimens (Blank-2). For the specimens with the wire mesh on which tannic acid coating was protected by cement slurry, reasonably low corrosion rate has been observed for 3% and 5% dose. For other combinations, the corrosion rate is higher but continues to be much lower than the control specimens (Blank-2).

6.5.2.3 PENETRATION RATE

The effect of variation of exposure duration on penetration rate has been presented in Tables– 6.3 and Table– 6.4 and shown in Figs. 6.21 – 6.22. The penetration rate trend is similar to that of corrosion rate. The penetration rate remains well within the acceptable limit for calcium nitrite and tannic acid inhibited medium for whole of the exposure duration except for the 1% dose of tannic acid (SW II-1) in saline water medium. For both the combinations of the calcium nitrite inhibited specimens exposed in potable water (NW I and NW SC I), the values of penetration rate (< 2 *μm/yr*) indicate perfectly passive state except for 1% dose where after 360 *days* of exposure, value of penetration rate is 4.028 *μm/yr* which is falls in the range 2 – 6 *μm/yr i.e.* the range of low to moderate corrosion (Law *et al.*, 2003). For the tannic acid inhibited specimens cast with the wire mesh coated with tannic acid film and protected with the cement slurry (NW SC II), the values of penetration rate are marginally above 2.0 *μm/yr*, indicating good corrosion inhibition. For all other combination of tannic acid in both the potable and saline water exposure medium, penetration rate falls in the range 2 – 6 *μm/yr* except for the 1% dose in saline water (SW II-1), thus indicating a fairly good corrosion inhibition.

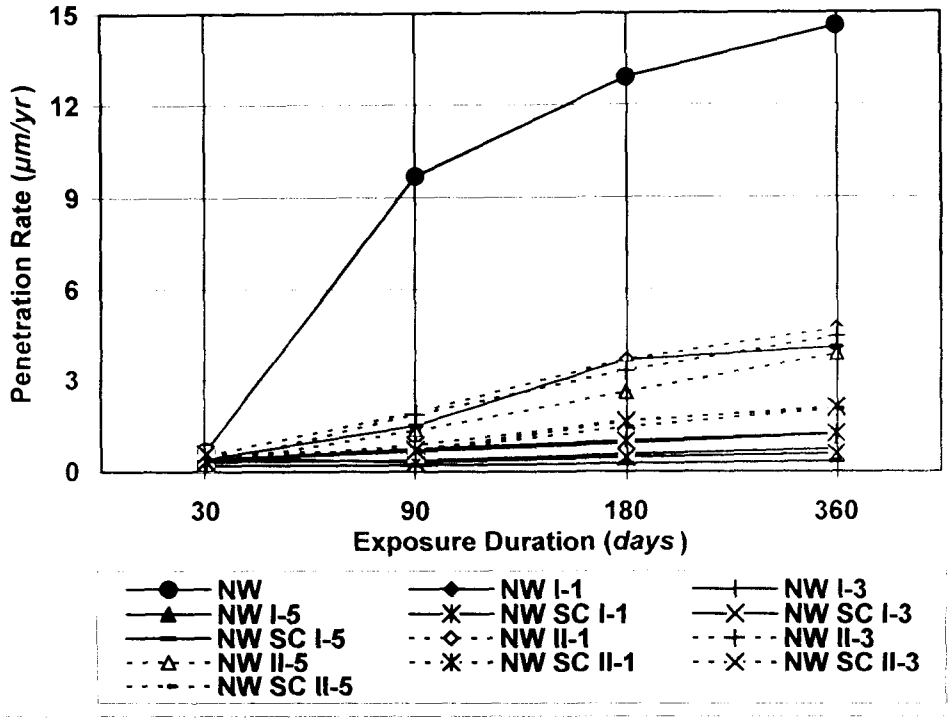

Fig. 6.21 Penetration Rate for Outer Layer Wire Mesh of Ferrocement Cuboids in Potable Water Medium

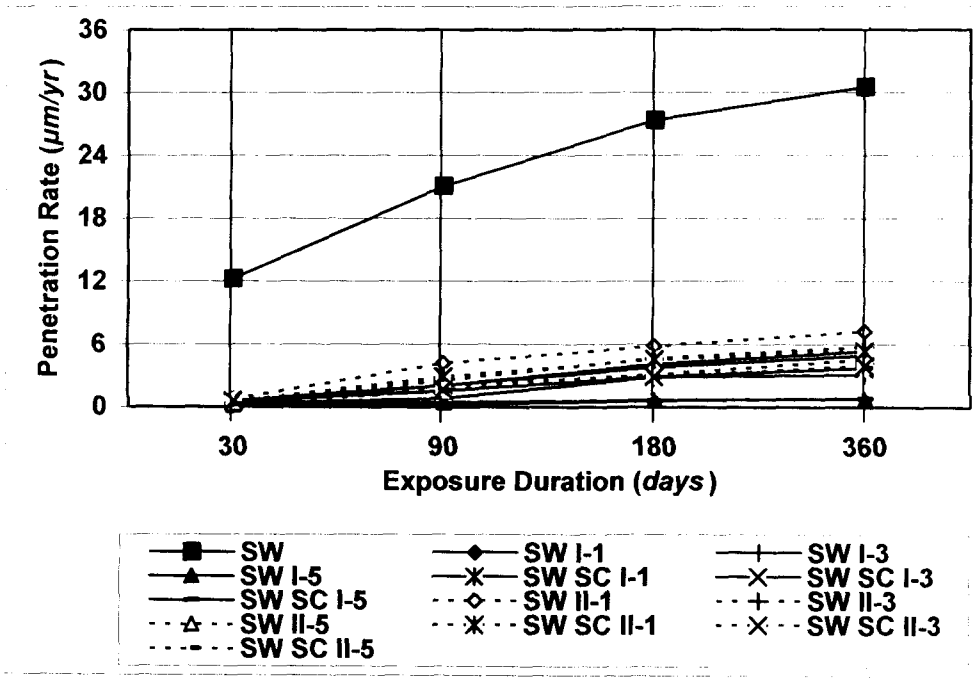

Fig. 6.22 Penetration Rate for Outer Layer Wire Mesh of Ferrocement Cuboids in Saline Water Medium

6.5.3 VISUAL INSPECTION

Some of the welded steel wire mesh specimens, taken out from cuboids after 360 *days* of exposure, have been shown in Figs. 6.23 – 6.30. Each photograph contains one blank specimen and three inhibited specimens with varying dose of inhibitors. As can be seen in Figs. 6.23 – 6.26, for the Blank-1 specimens in the potable water medium, non-uniform corrosion covering almost entire surface has been observed. For the Blank-2 specimens in the saline water medium, as shown in Figs. 6.27 – 6.30, high corrosion covering full surface has been noticed.

It has been observed that the calcium nitrite inhibited specimens (NW I and NW SC I) have no sign of corrosion for 3% and 5% dose. For 1% dose, only some localized spots can be seen (Figs. 6.23 – 6.24). Non-traceable to a very few isolated spots of corrosion were found in specimens inhibited with calcium nitrite and exposed in saline water medium at 3% and 5% dose of inhibitor (SW I and SW SC I). However, for 1% dose of calcium nitrite inhibitor in saline water medium, mild surface corrosion spread over almost 40-50% of the surface area has been observed (SW I-1) as can be seen in Figs. 6.27 – 6.28.

In case of specimens having coating of tannic acid and exposed in potable water (NW II) some isolated spots of corrosion can be seen (Figs. 6.25 – 6.26). In specimens exposed to saline water medium (SW II), slightly more spots of corrosion as compared to that found in potable water medium are observed (Figs. 6.29 – 6.30). The other type of specimens having cement slurry protection over the surface (NW SC II and SW SC II) have performed well as compared to specimens having coatings of tannic acid only. This observation have been made because either the corrosion is non-traceable or a very few isolated spots of corrosion has been noticed over the surface of this type of corrosion. The visual observations therefore validate the findings reported earlier.

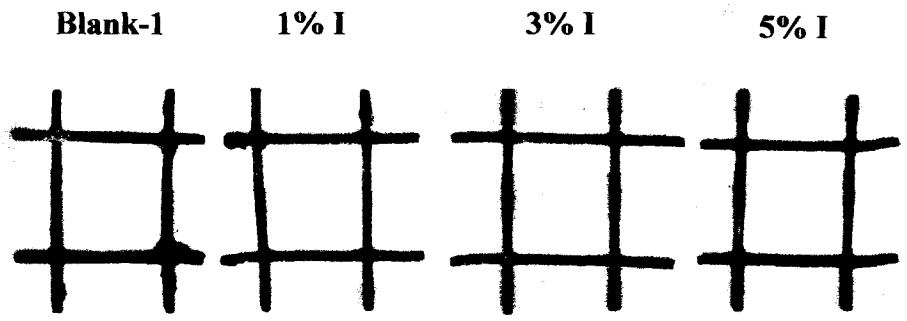

Fig. 6.23 Wire Mesh Specimen Embedded in Ferrocement Cuboids cast with Calcium Nitrite Inhibited Mortar after 360 *days* of Exposure in Potable Water Medium (Blank and Calcium Nitrite Inhibited – NW I)

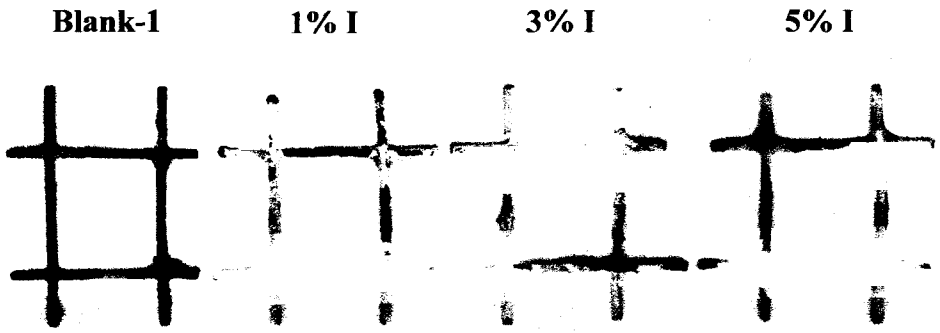

Fig. 6.24 Wire Mesh Specimen with Calcium Nitrite Inhibited Cement Slurry Coat Embedded in Ferrocement Cuboids after 360 *days* of Exposure in Potable Water Medium (Blank and Calcium Nitrite Inhibited – NW SC I)

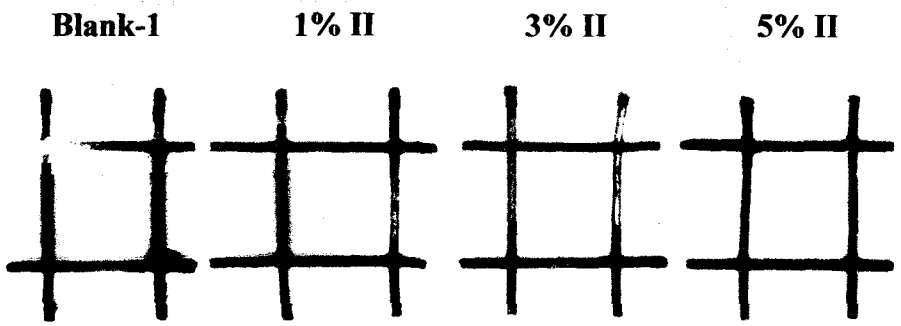

Fig. 6.25 Wire Mesh Specimen with Tannic Acid Coating Embedded in Ferrocement Cuboids after 360 *days* of Exposure in Potable Water Medium (Blank and Tannic Acid Inhibited – NW II)

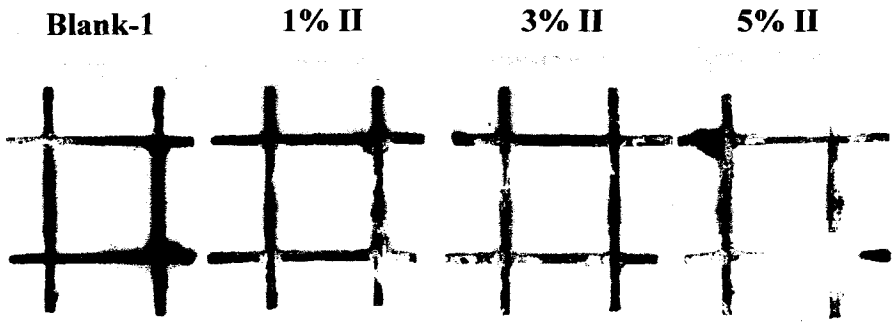

Fig. 6.26 Wire Mesh Specimen with Cement Slurry Coat over Tannic Film after 360 *days* of Exposure in Potable Water Medium (Blank and Tannic Acid Inhibited – NW SC II)

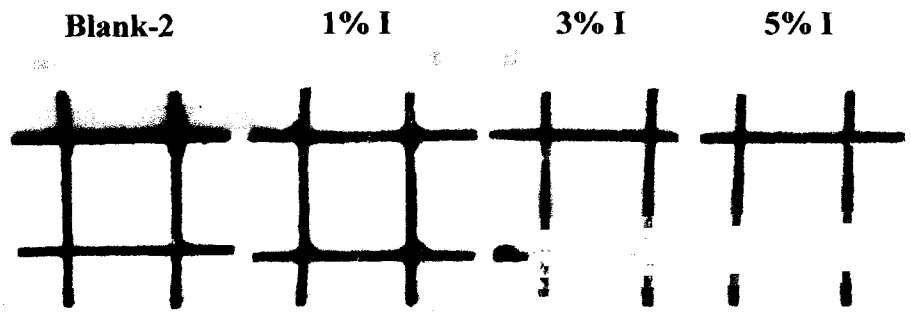

Fig. 6.27 Wire Mesh Specimen Embedded in Ferrocement Cuboids cast with Calcium Nitrite Inhibited Mortar after 360 *days* of Exposure in Saline Water Medium (Blank and Calcium Nitrite Inhibited – SW I)

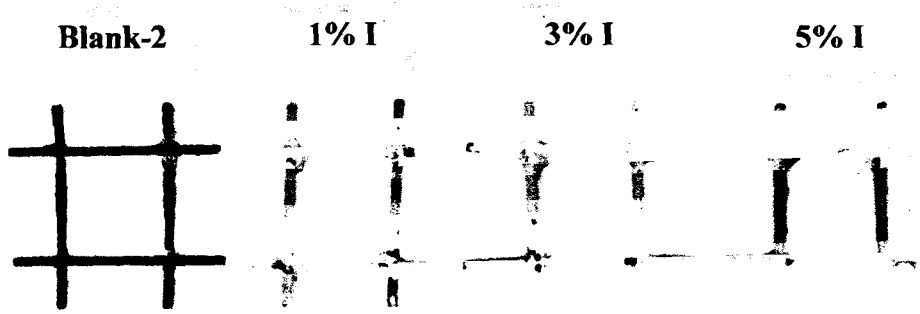

Fig. 6.28 Wire Mesh Specimen with Calcium Nitrite Inhibited Cement Slurry Coat Embedded in Ferrocement Cuboids after 360 *days* of Exposure in Saline Water Medium (Blank and Calcium Nitrite Inhibited – SW SC I)

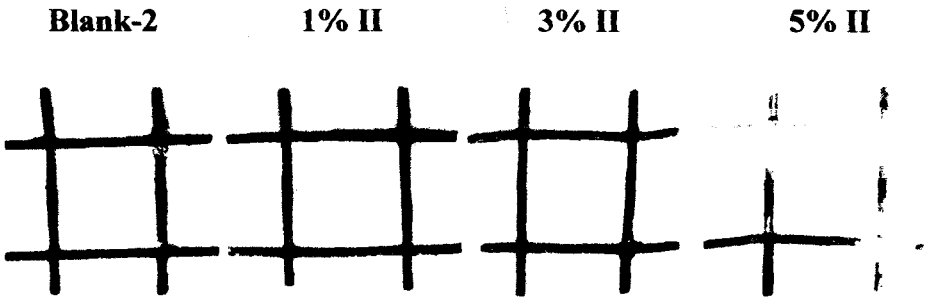

Fig. 6.29 Wire Mesh Specimen with Tannic Acid Coating Embedded in Ferrocement Cuboids after 360 *days* of Exposure in Saline Water Medium (Blank and Tannic Acid Inhibited – SW II)

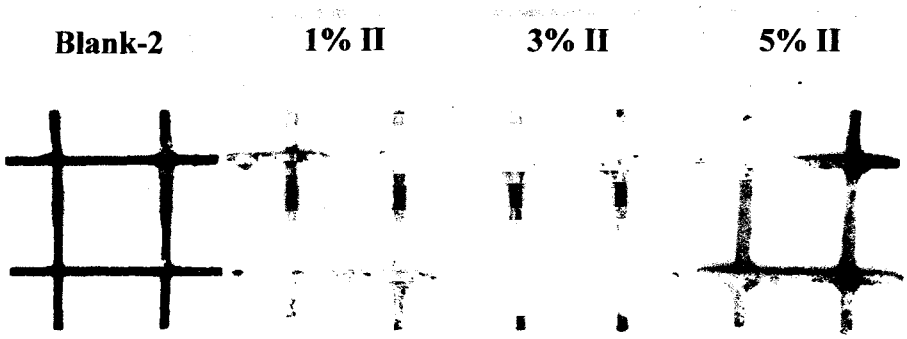

Fig. 6.30 Wire Mesh Specimen with Cement Slurry Coat over Tannic Film after 360 *days* of Exposure in Saline Water Medium (Blank and Tannic Acid Inhibited – SW SC II)

6.6 EVALUATION OF CORROSION IN INNER WIRE MESH LAYER

Various investigators have concluded that mortar cover to the wire mesh reinforcement in ferrocement is an important parameter which improves the durability. Several investigators have reported that relatively thicker mortar cover to the mesh reinforcement in ferrocement, improves the resistance against corrosion (Turner, 1983; Chowdhury and Nimityongskul, 1985; Lukita, Austriaco and Nimityongskul, 1987; Alexander, 1989; Ramesht, Vickridge and Jafer, 1993; Vickridge and Ranjbar, 1998).

In this section, an attempt has been made to compare the extent of corrosion in the outer wire mesh layer having a cover of 6 *mm* with the corrosion in the inner wire mesh layer situated at a depth of 12 *mm* from the outer most surface of plate; vis-à-vis the effectiveness of the mesh location from the outer most surface, in preventing the ingress of corrosion activity in the wire mesh layers. The percentage variation in weight loss, corrosion inhibition efficiency, corrosion rate and penetration rate for both the outer and inner wire mesh layers have been presented in Table– 6.7 and Table– 6.8 and also shown in Figs. 6.31 – 6.36.

It is clearly evident from Table– 6.7 that for nearly all the specimens, weight loss in internal wire mesh layer is lower than the external wire mesh layer thus indicating the effect of the thickness of cover in resisting corrosion. However, only for one specimen *i.e.* SW I-1, the weight loss is only fractionally higher in internal layers of wire mesh as compared to the external wire mesh layer. Probably the higher Cl^-/NO_2^- ratio is the main reason behind this accelerated corrosion activity in the inner wire mesh layers.

Their seems to be apparently no significant change in the corrosion efficiency for the inner wire mesh layers owing to the lower weight loss values observed for inner wire mesh layers as compared to the outer wire mesh layers, which ultimately corresponds to more or a less a similar corrosion efficiency level for both the layers. However, for the inner wire mesh layers, the corrosion rate and the penetration rate values indicate a reduction to the tune of 8 – 15% as compared to outer most wire mesh layer with a single exception of the specimen SW I-1.

Table– 6.7 Comparison of Average Weight Loss and Corrosion Inhibition Efficiency of Outer and Inner Wire Mesh Layer Embedded Inside Ferrocement Cuboids

Systems of Exposure	Average Weight Loss in Outer Mesh (*mg*)	Average Weight Loss in Inner Mesh (*mg*)	% Variation in Weight loss	Efficiency for Outer Mesh (%)	Efficiency for Inner Mesh (%)	% Variation in Efficiency
NW	70.333	59.60	15.26	---	---	---
NW I-1	19.783	17.633	10.87	71.87	70.41	2.03
NW I-3	5.900	5.067	14.12	91.61	91.50	0.15
NW I-5	3.516	3.100	11.83	95.00	94.80	0.21
NW SC I-1	6.061	5.300	12.57	91.45	91.11	0.36
NW SC I-3	2.816	2.533	10.05	96.00	95.75	0.26
NW SC I-5	1.583	1.367	13.64	97.75	97.71	0.04
NW II-1	22.650	20.330	10.24	67.78	65.89	1.93
NW II-3	21.416	18.400	14.08	69.55	69.13	0.60
NW II-5	18.600	16.133	13.26	73.55	72.93	0.84
NW SC II-1	9.916	8.633	12.94	85.90	85.51	0.45
NW SC II-3	10.183	9.000	11.62	85.52	84.90	0.72
NW SC II-5	9.783	8.667	11.41	86.09	85.46	0.73
SW	147.200	138.567	5.86	---	---	---
SW I-1	26.016	27.000	-3.78	82.33	80.51	2.21
SW I-3	15.167	14.333	5.50	89.70	89.66	0.05
SW I-5	3.933	3.400	13.55	97.33	97.55	-0.23
SW SC I-1	24.050	21.267	11.57	83.66	84.65	-1.18
SW SC I-3	18.133	15.900	12.31	87.68	88.52	-0.96
SW SC I-5	4.150	3.500	15.66	97.18	97.47	-0.30
SW II-1	35.033	31.138	11.12	76.20	77.53	-1.74
SW II-3	28.100	25.367	9.72	80.91	81.69	-0.96
SW II-5	22.067	19.300	12.54	85.00	86.07	-1.26
SW SC II-1	26.100	22.333	14.43	82.27	83.88	-1.96
SW SC II-3	19.183	16.333	13.29	86.97	88.00	-1.18
SW SC II-5	18.516	16.067	13.23	87.42	88.40	-1.12

Table– 6.8 Comparison of Corrosion Rate and Penetration Rate of Outer and Inner Wire Mesh Layer Embedded Inside Ferrocement Cuboids

Systems of Exposure	Corrosion Rate in Outer Mesh (*mpy*)	Corrosion Rate in Inner Mesh (*mpy*)	% Variation in Corrosion Rate	Penetration Rate for Outer Mesh (*μm/yr*)	Penetration Rate for Inner Mesh (*μm/yr*)	%Variation in Penetration Rate
NW	0.574	0.487	15.16	14.580	12.370	15.16
NW I-1	0.161	0.144	10.56	4.089	3.658	10.54
NW I-3	0.048	0.041	14.58	1.219	1.041	14.60
NW I-5	0.029	0.025	13.79	0.737	0.635	13.84
NW SC I-1	0.049	0.043	12.24	1.245	1.092	12.29
NW SC I-3	0.023	0.021	8.70	0.584	0.533	8.73
NW SC I-5	0.013	0.011	15.38	0.330	0.279	15.45
NW II-1	0.185	0.166	10.27	4.699	4.216	10.28
NW II-3	0.175	0.150	14.29	4.445	3.810	14.29
NW II-5	0.152	0.132	13.16	3.861	3.353	13.16
NW SC II-1	0.081	0.070	13.58	2.057	1.778	13.56
NW SC II-3	0.083	0.073	12.05	2.108	1.854	12.05
NW SC II-5	0.080	0.071	11.25	2.032	1.803	11.27
SW	1.202	1.132	5.82	30.531	28.753	5.82
SW I-1	0.212	0.220	-3.77	5.385	5.588	-3.77
SW I-3	0.124	0.117	5.64	3.150	2.972	5.65
SW I-5	0.032	0.028	12.50	0.813	0.711	12.55
SW SC I-1	0.196	0.174	11.22	4.978	4.420	11.21
SW SC I-3	0.148	0.130	12.16	3.760	3.302	12.18
SW SC I-5	0.034	0.029	14.70	0.864	0.748	13.43
SW II-1	0.286	0.254	11.19	7.264	6.452	11.18
SW II-3	0.229	0.207	9.61	5.817	5.258	9.61
SW II-5	0.180	0.158	12.22	4.572	4.013	12.22
SW SC II-1	0.213	0.182	14.55	5.410	4.623	14.55
SW SC II-3	0.157	0.136	13.37	3.988	3.454	13.39
SW SC II-5	0.151	0.131	13.24	3.835	3.327	13.25

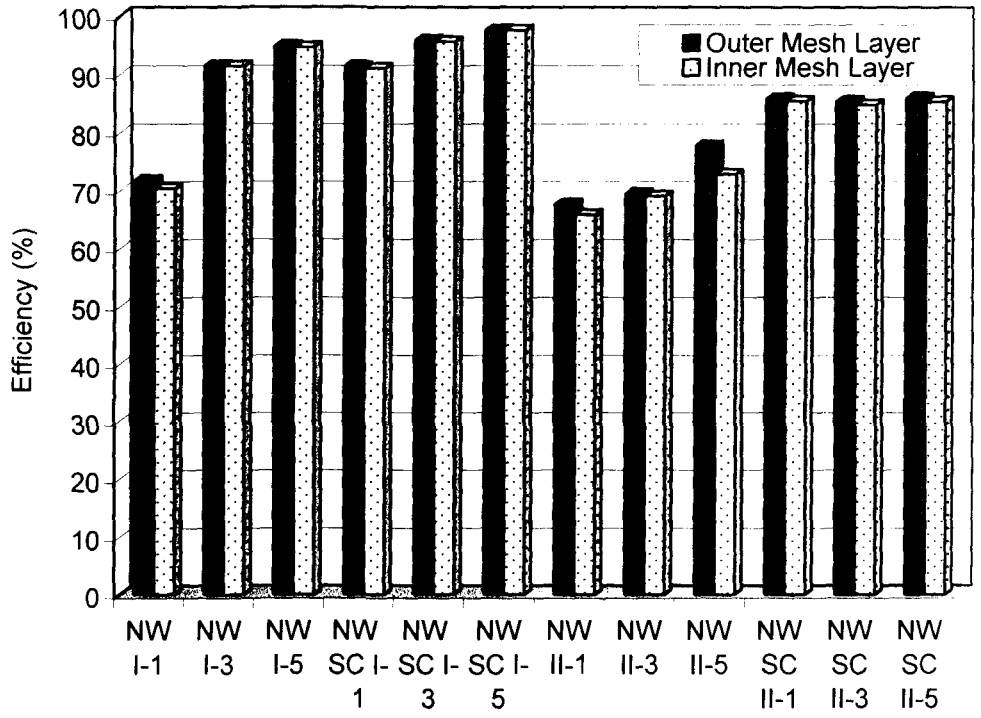

Fig. 6.31 Comparison of Efficiency for Outer and Inner Mesh in Ferrocement Cuboid Specimens Exposed in Potable Water

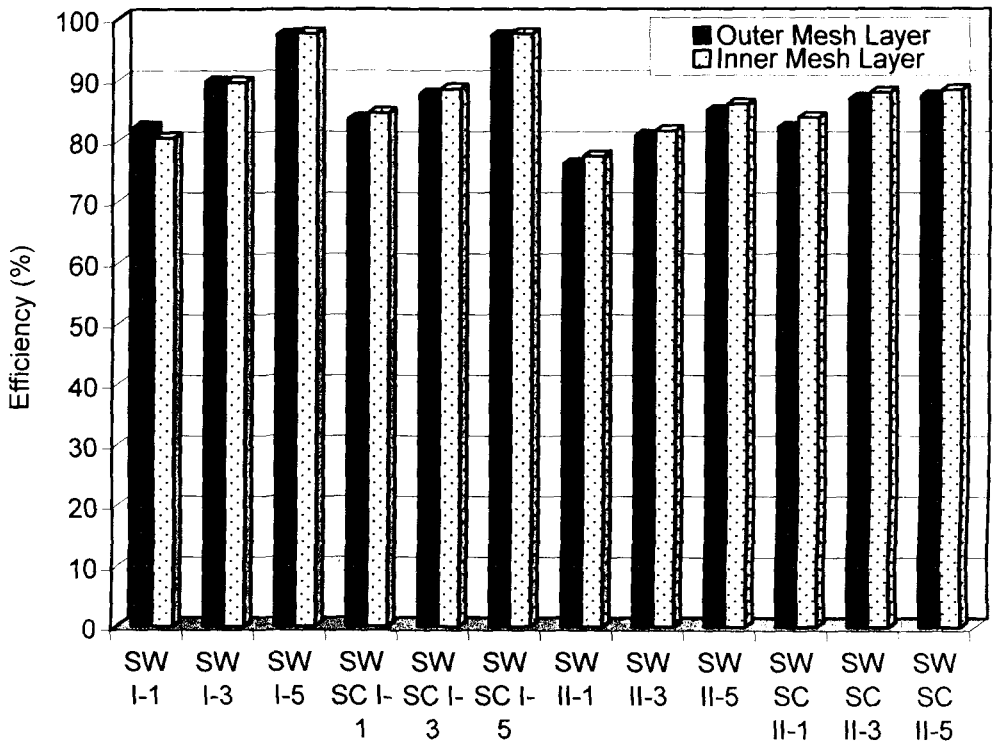

Fig. 6.32 Comparison of Efficiency for Outer and Inner Mesh in Ferrocement Cuboid Specimens Exposed in Saline Water

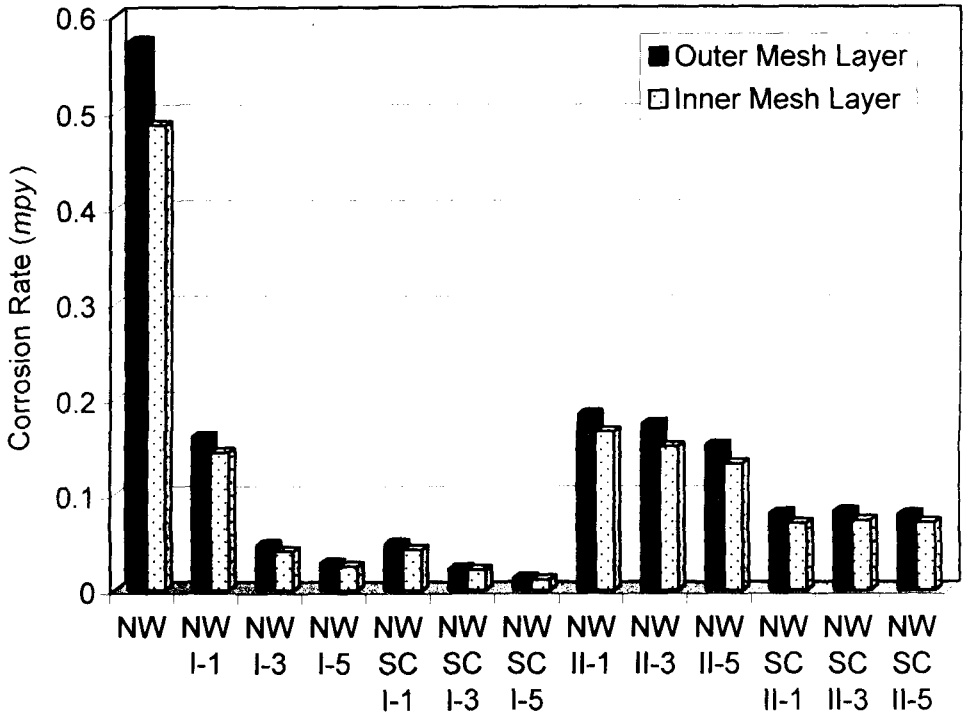

Fig. 6.33 Comparison of Corrosion Rate of Outer and Inner Mesh in Ferrocement Cuboid Specimens Exposed in Potable Water

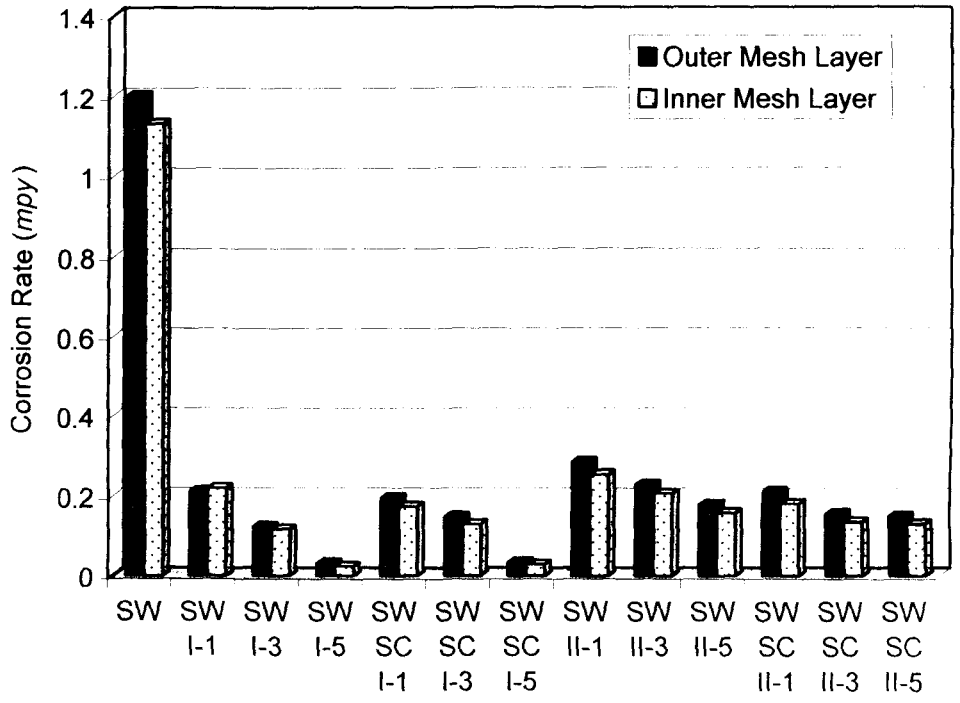

Fig. 6.34 Comparison of Corrosion Rate of Outer and Inner Mesh in Ferrocement Cuboid Specimens Exposed in Saline Water

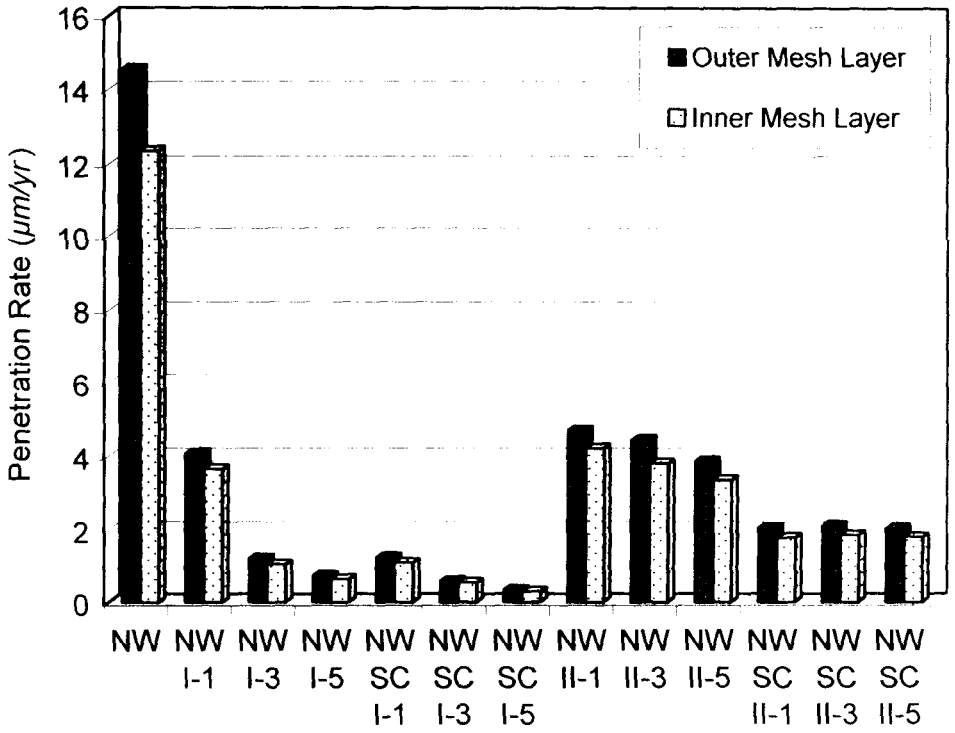

Fig. 6.35 Comparison of Penetration Rate of Outer and Inner Mesh Layers in Ferrocement Cuboid Specimens Exposed in Potable Water

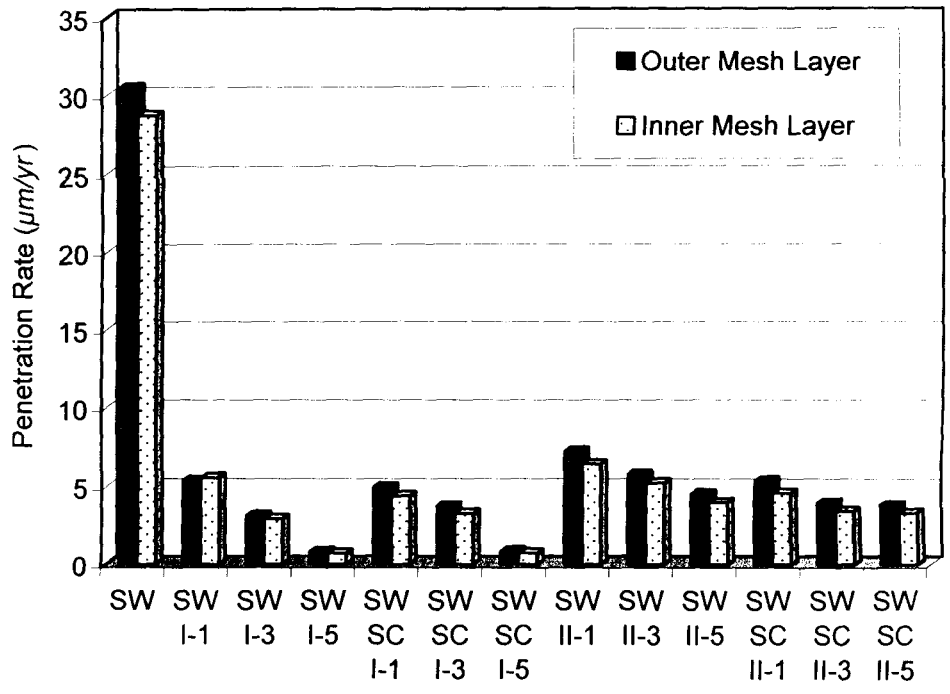

Fig. 6.36 Comparison of Penetration Rate of Outer and Inner Mesh Layers in Ferrocement Cuboid Specimens Exposed in Saline Water

6.7 ENHANCEMENT IN DURABILITY

The main objective of the present study is to improve the durability of the ferrocement composite by protecting the wire mesh layers, embedded inside the mortar layers, from the corrosion ingress. The irony behind the corrosion phenomenon is that it not only reduces the effective cross sectional area of the steel but also deteriorates the composite as a whole since the bond between the reinforcement and the matrix gets weakened. In this investigation, therefore, an attempt has been made to quantify the corrosion in the wire meshes exposed in the simulated saline environment. The protection provided to the reinforcement by the corrosion inhibitors, applied in different ways as described in the scheme of investigation and presented in Table– 6.2, can be assessed in terms of the various corrosion parameters *viz.* corrosion efficiency, corrosion rate and penetration rate.

Since the penetration rate clearly reveals the rate of depletion of reinforcement over a period of time, it can further be used to study another important parameter *viz.* 'durability factor'. The ratio of the penetration rate for the control specimen and the inhibited specimen is called as durability factor and for a particular corrosion inhibitor; it gives an idea about the relative effectiveness of that inhibitor and also its application methodology. In nutshell, durability factor provides some inputs regarding the life of the reinforcement. The durability factor for control and inhibited specimens is presented in the Table– 6.9.

The values of the durability factors, obtained for outer and inner wire mesh layers embedded in ferrocement cuboids specimens, clearly indicate the effectiveness of the various combinations of corrosion inhibitors and its application methodology. In the specimens exposed in potable water medium, durability factor as high as 44.183 for specimens (NW SC I-5) has been obtained for outer wire mesh layer. The lowest value of the durability factor has been found as 3.103 for specimens (NW II-1). In saline water exposure medium, the corresponding values have been found to be 37.553 for specimens (SW I-5) and 4.203 for the specimens (SW II-1). For the inner layers of wire mesh, the maximum and minimum durability factor values have been obtained as 44.337 for specimens (NW SC I-5) and 2.934 for specimens (NW II-1) respectively in potable water medium; and in saline water medium these values have been observed to be 40.440 for specimens (SW I-5) and 4.456 for specimens (SW II-1) respectively.

Table– 6.9 Durability Factor for Outer and Inner Wire Mesh Layers Embedded inside Ferrocement Cuboids

S. No.	Systems of Exposure	Penetration Rate for Outer Mesh (*μm/yr*)	Durability Factor for Outer Mesh	Penetration Rate for Inner Mesh (*μm/yr*)	Durability Factor for Inner Mesh
1.	NW	14.580	---	12.370	---
2.	NW I-1	4.089	3.566	3.658	3.382
3.	NW I-3	1.219	11.961	1.041	11.883
4.	NW I-5	0.737	19.783	0.635	19.480
5.	NW SC I-1	1.245	11.711	1.092	11.328
6.	NW SC I-3	0.584	24.966	0.533	23.208
7.	NW SC I-5	0.330	44.183	0.279	44.337
8.	NW II-1	4.699	3.103	4.216	2.934
9.	NW II-3	4.445	3.280	3.810	3.247
10.	NW II-5	3.861	3.776	3.353	3.689
11.	NW SC II-1	2.057	7.088	1.778	6.957
12.	NW SC II-3	2.108	6.916	1.854	6.672
13.	NW SC II-5	2.032	7.175	1.803	6.861
14.	SW	30.531	---	28.753	---
15.	SW I-1	5.385	5.698	5.588	5.145
16.	SW I-3	3.150	9.692	2.972	9.675
17.	SW I-5	0.813	37.553	0.711	40.440
18.	SW SC I-1	4.978	6.133	4.420	6.505
19.	SW SC I-3	3.760	8.120	3.302	8.708
20.	SW SC I-5	0.864	35.337	0.748	38.440
21.	SW II-1	7.264	4.203	6.452	4.456
22.	SW II-3	5.817	5.248	5.258	5.468
23.	SW II-5	4.572	6.678	4.013	7.165
24.	SW SC II-1	5.410	5.643	4.623	6.219
25.	SW SC II-3	3.988	7.656	3.454	8.325
26.	SW SC II-5	3.835	7.961	3.327	8.624

The values of durability factor clearly indicate a significant increase in the effective life of the inhibited specimens due to the protection provided by the corrosion inhibitors. Enhancement in life due to the calcium nitrite inhibited environment either in the form of inhibited mortar (NW I and SW I) or inhibited cement slurry coat (NW SC I and SW SC I) is exceptionally high. Tannic acid has also provided sufficiently high enhancement in life especially when the tannic acid film has been protected by the cement slurry (NW SC II and SW SC II). In case of un-protected coating of tannic acid (NW II and SW II), enhancement of life has been obtained at higher dose of inhibitor only.

6.8 CONCLUDING REMARKS

In the present Chapter an attempt has been made to investigate the effectiveness of the two corrosion inhibitors namely calcium nitrite and tannic acid in controlling/delaying the corrosion in wire meshes embedded inside the ferrocement cuboids subjected to alternate drying and wetting under potable and saline water medium over a period of 360 *days*. The investigation was also aimed at exploring the best inhibitor application methodology. Both the inhibitors were used in two different ways. Calcium nitrite was once mixed directly into the mix and in the second case inhibited cement slurry was prepared which was applied over the surface of the wire meshes. The other inhibitor *i.e.* tannic acid was once applied in the form of thin film over the wire mesh layer whereas in the second case this film was further protected by the cement slurry coating. The dose of the inhibitors was varied as 1%, 3% and 5%.

Calcium nitrite has exhibited extremely high corrosion inhibition with all the combinations used for the specimens exposed in potable water medium. For 3% and 5% dose of calcium nitrite in both the situations *i.e.* when it has been mixed with the mortar (NW I) or when applied in the form of inhibited cement slurry (NW SC I), a perfect passive state has been achieved even after 360 *days* of exposure. It is further substantiated from the visual inspection also where the wire meshes are found to be absolutely free from any signs of corrosion initiation. Even for 1% dose applied in the form of the inhibited cement slurry (NW SC I-1), similar level of inhibition has been achieved as that exhibited at higher doses.

When directly mixed with mortar at 1% dose of calcium nitrite (NW I-1), although the level of inhibition is not that high but still it remains within the acceptable limits. Visual inspection of these specimens further validates these findings.

In saline water exposure medium, 5% dose of calcium nitrite gives the absolute passive state for both the application methodologies (SW I and SW SC I). Even at 3% dose, quite high inhibition has been obtained. The specimen having 5% dose of calcium nitrite has not shown any signs of corrosion. Only some spots of corrosion initiation have been visible over the surface of the specimen at 3% dose. For 1% dose, the inhibition is little low but that too remains in acceptable limits.

Within the two modes of application of calcium nitrite, the one where the inhibitor is applied in the form of inhibited cement slurry (NW SC I and SW SC I), appears to perform better since the inhibitor in high concentration, is in close contact with the reinforcement. The advantages of applying calcium nitrite in slurry coated form is that it neither affects the setting time of the cement and nor it influences the chemical reactions which take place during the process of hydration and hardening. Another advantage is the cost effectiveness of this application technique, since in both the modes of application calcium nitrite has been added by the weight of the cement. In the first case where it has been used in the matrix, the amount of the calcium nitrite is much higher as it is added by the total weight of cement needed to cast a particular specimen whereas in the second case where only the inhibited cement slurry has to be used to form the coating over the surface of reinforcement, a very little amount of inhibitor is required for the similar dose of inhibitor as very small amount of slurry can form the inhibited coating over the surface of reinforcement required to cast a specimen.

For the tannic acid, however, the best results have been obtained for the specimens where the tannic acid film over the wire mesh was protected further by the cement slurry coating (NW SC II and SW SC II). Effect of increase in the dose of tannic acid seems to be very marginal for specimens in this category. In potable water exposure medium, the level of inhibition exhibited by all the doses is extremely high. In saline water medium, however, 3% and 5% doses have shown high inhibition whereas at 1% dose the inhibition is not that high.

For the specimens where the tannic acid film has been formed over the surface of wire meshes and no protection has been provided (NW II and SW II), only at 5% dose the results are satisfactory. At lower dose, relatively low corrosion inhibition has been obtained. The reason behind the ineffectiveness of the tannic acid in the form of film without the protection of the cement slurry coating is its dissolution in the presence of diluents. When water percolates and reaches up to the surface of the reinforcement, it appears that the tannic acid coating dissolves with the passage of time, thus leaving a depleted protective passivating layer. Visual examination of the specimens of this category also confirms the above findings.

As the weight loss in the inner layer of wire mesh is only marginally less than the outer layer of the wire mesh, it can be fairly concluded that even a higher mortar thickness available for the inner wire meshes, provides only a little relief from corrosion. It is, therefore, pertinent here to plan out strategies for the corrosion protection of both outer and inner wire mesh layers.

Very high durability factor has been obtained for most of the calcium nitrite inhibited specimens, which clearly indicates its effectiveness in enhancing the life of the reinforcement used in the form of meshes. Even for the tannic acid, except for a few of the combinations, reasonably high durability factor has been observed.

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Chapter 7

Flexural Tests on Ferrocement Plates

7.1 GENERAL

In the preceding chapters investigations aimed at selection of most appropriate corrosion inhibitors and their application methodologies have been presented. After having arrived at some meaningful conclusions, it was felt necessary to validate these already tested corrosion inhibition strategies on scaled ferrocement plate specimens to further examine and establish their effectiveness in mitigating and controlling corrosion. It was with this objective, 78 ferrocement plate specimens were cast with varying doses of corrosion inhibitors and the application methodologies as used earlier. All the ferrocement plate specimens were exposed to dry and wet cycles for a period of 360 *days*. These specimens were tested in flexure to ascertain the effect of corrosion inhibitors on their load-deflection behaviour and characteristics up to the failure level.

7.2 DETAILS OF EXPERIMENTAL SCHEME

Ferrocement plate specimens of size 370×150×24 *mm* were cast as per the investigation scheme presented in Table– 7.1. Welded wire meshes were embedded inside mortar in three layers in a similar manner as used for the ferrocement cuboids specimens. It was decided to continue with all the combinations of dose of inhibitors and application methodologies as used in Chapter-6 for the ferrocement cuboid specimens. Both the corrosion inhibitors *viz.* Calcium nitrite and Tannic acid were used in 1%, 3% and 5% dose. Here also calcium nitrite was used in two forms. In the first case, it was mixed directly into the cement sand mortar by weight of cement. In the second case, it was

mixed in cement slurry by weight of cement and the resulting paste was used to form a coating of this inhibited cement slurry over the wire mesh surface. Tannic acid was also used in two ways. In the first case, coating of tannic acid was directly formed as a thin film over the wire mesh as explained in Section- 5.3. In the second mode of application a protective coating of plain cement slurry was applied over the film of tannic acid. The details of the investigation scheme are given in Table– 7.1. For each exposure medium specimens were cast in triplicate.

7.3 CONSTITUENT MATERIALS

The properties of the constituent materials *viz.* cement, sand, water and wire mesh, used for casting of the ferrocement plate specimens are given below.

7.3.1 CEMENT

Ordinary Portland cement of 43 Grade was used. The physical properties of the cement were determined in the laboratory as per, IS: 269; IS: 8112-1989 and IS: 4031(Part 5 & 6)-1988 and given in the Chapter-4 (Table- 4.2).

7.3.2 SAND

Locally available coarse sand was used for casting all the plate specimens. The grading of the sand is given in Chapter-4 (Table- 4.3). The fineness modulus of the sand was found to be 2.30.

7.3.3 WATER

Potable water was used for mixing and curing of specimens. The properties of the potable water used for the present study is given in Chapter-4 (Table- 4.4).

7.3.4 WIRE MESH

Welded steel wire mesh pieces were cut in requisite size from wire mesh rolls of size 0.92×7.5 *m*. The wire meshes were tested in in-plane tension as shown in Fig. 7.1. The details of wire mesh geometry and the values of yield stress; ultimate stress and Young's modulus for the welded steel wire mesh were determined and given in Table– 7.2.

Table– 7.1 Investigation Scheme for Tests on Ferrocement Plates

S. No.	Exposure Medium	Dose of Inhibitor (%)	Specimens Designation	Duration of Exposure (*days*)
1.	Potable Water (Blank-1)	0	PNW (Control)	360
2.	Potable Water with Inhibitor Type–I (Calcium Nitrite Mixed in Mortar)	1	PNW I-1	360
3.		3	PNW I-3	360
4.		5	PNW I-5	360
5.	Potable Water with Inhibitor Type–I (Calcium Nitrite in Slurry Coated Form)	1	PNW SC I-1	360
6.		3	PNW SC I-3	360
7.		5	PNW SC I-5	360
8.	Potable Water with Inhibitor Type–II (Tannic Acid Coating)	1	PNW II-1	360
9.		3	PNW II-3	360
10.		5	PNW II-5	360
11.	Potable Water with Inhibitor Type–II (Tannic Acid Coating Protected with Cement Slurry)	1	PNW SC II-1	360
12.		3	PNW SC II-3	360
13.		5	PNW SC II-5	360
14.	Saline Water (Blank-2)	0	PSW (Control)	360
15.	Saline Water with Inhibitor Type–I (Calcium Nitrite Mixed in Mortar)	1	PNW I-1	360
16.		3	PNW I-3	360
17.		5	PNW I-5	360
18.	Saline Water with Inhibitor Type–I (Calcium Nitrite in Slurry Coated Form)	1	PNW SC I-1	360
19.		3	PNW SC I-3	360
20.		5	PNW SC I-5	360
21.	Saline Water with Inhibitor Type–II (Tannic Acid Coating)	1	PNW II-1	360
22.		3	PNW II-3	360
23.		5	PNW II-5	360
24.	Saline Water with Inhibitor Type–II (Tannic Acid Coating Protected with Cement Slurry)	1	PNW SC II-1	360
25.		3	PNW SC II-3	360
26.		5	PNW SC II-5	360

Table– 7.2 Properties of Wire Mesh

Description	Yield Stress (N/mm^2)	Ultimate Stress (N/mm^2)	Modulus of Elasticity (N/mm^2)
Welded Square Galvanized Mild Steel Mesh with Opening Size 16×16 *mm* and Average Wire Diameter of 1.42 *mm*	330	515	111535

7.4 CASTING OF FERROCEMENT PLATE SPECIMENS

Ferrocement plate specimens of size 370×150×24 *mm* were cast by embedding three layers of the wire meshes in virgin and inhibited states as explained in the section 7.2, in 6 *mm* thick mortar layers leaving a minimum outer cover of 6 *mm* available to the exterior mesh on either side. The mould used for the casting of the cuboids is shown in Fig. 7.2. It comprises of four flats of Perspex on each side held in position over a water proof ply board wooden base plate with the help of steel nuts and bolts. The thickness of each flat was 6 *mm*. Initially one flat each, on all four sides, were held in position. The mortar was spread inside the mould such that a mortar layer of 6 *mm* was obtained. Then piece of wire mesh as shown in Fig. 7.3(a), was put in position. After that another set of four flats, one each at all four sides, were positioned and another layer of mortar was put in position. The second layer of wire mesh was put above this mortar layer. This process was repeated until a thickness of 24 *mm* was achieved. A typical ferrocement plate specimen is shown in Fig. 7.3(b).

7.5 WET AND DRY CYCLES OF EXPOSURE

The ferrocement plate specimens were exposed to alternate wetting and drying cycles comprising of 5 *days* of wetting followed by 5 *days* of drying in one cycle. Under the wet cycle of exposure, specimens were kept submerged in large plastic buckets while for the dry cycle, specimens were allowed to dry at room temperature of 28±2 *C*, as shown in Figs. 7.3(c,d).

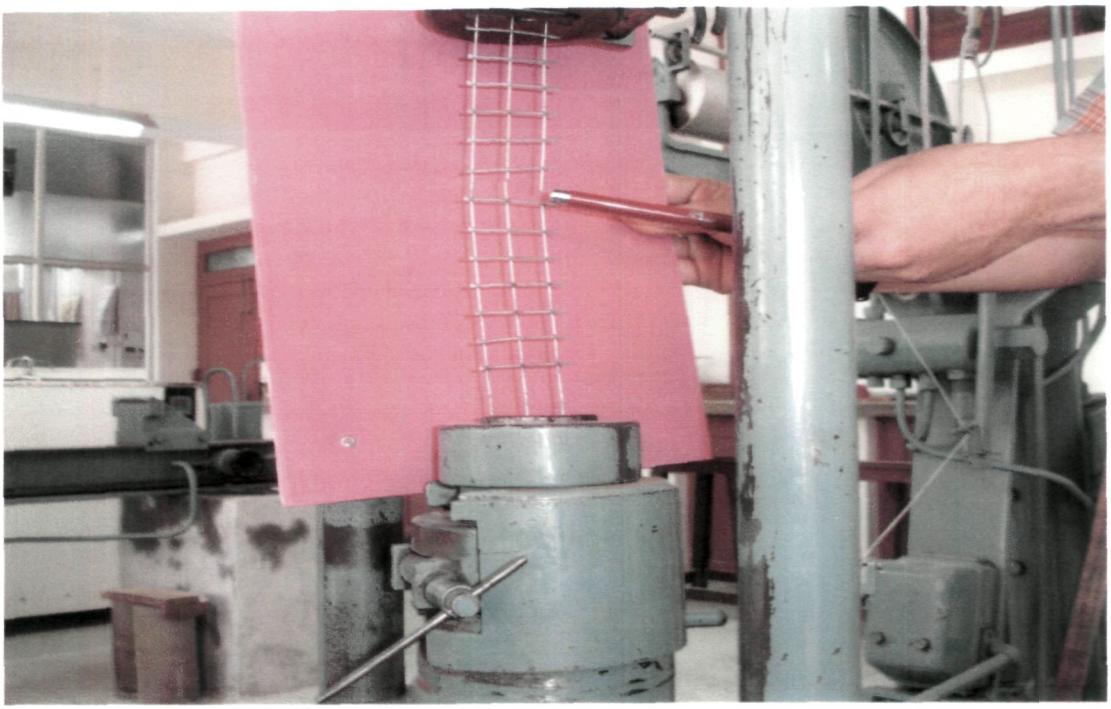


Fig. 7.1 Testing of Wire Mesh in In-plane Axial Tension

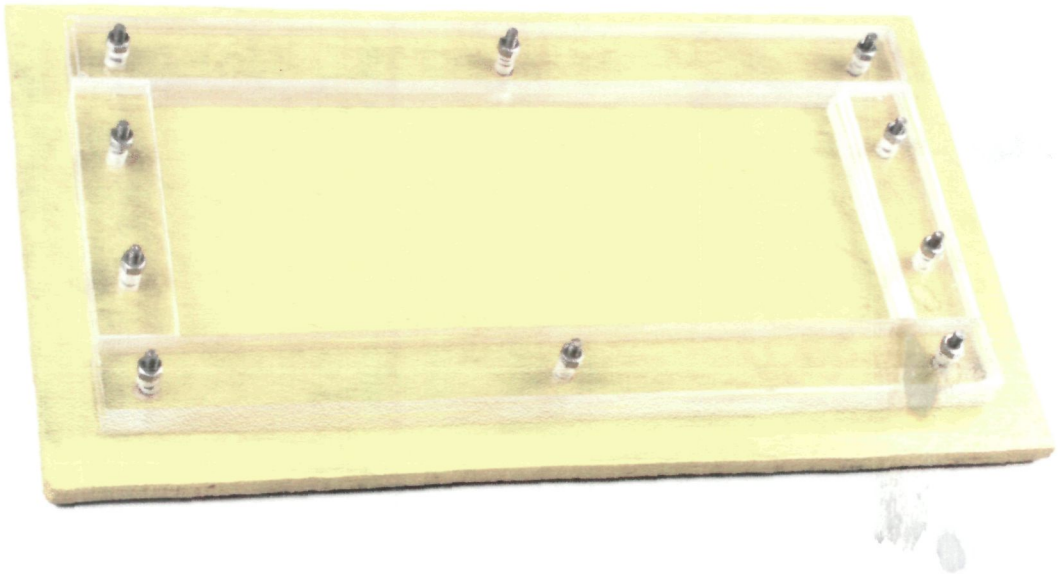


Fig. 7.2 Mould Used for the Casting of the Ferrocement Plate Specimens

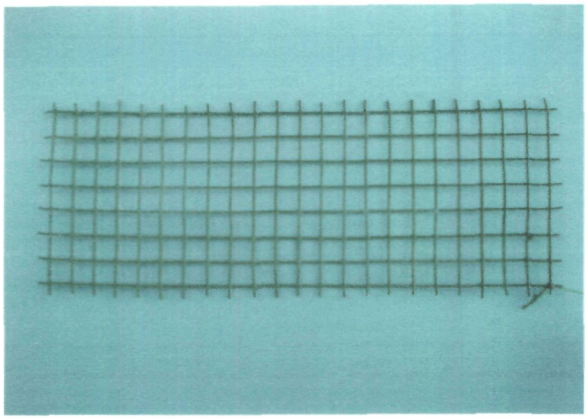
After 360 *days* of exposure, that is at the end of 36 wet and dry cycles, ferrocement plate specimens were taken out. The specimens were white washed in order to make the crack patterns as well the failure patterns clearly visible when subjected to test loads. A set of test specimens has been shown in Fig. 7.3(f).

7.6 TESTING OF FERROCEMENT PLATE SPECIMENS

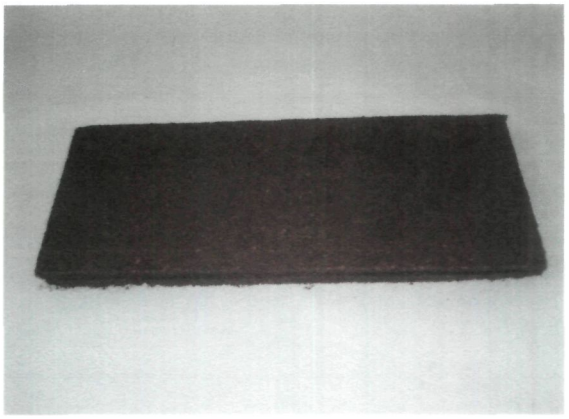
The ferrocement plate specimens were tested in INSTRON (Model-1342) Universal Testing Machine at the Institute Instrumentation Centre, Indian Institute of Technology (IIT), Roorkee, India, under controlled displacement condition at a rate of 0.5 *mm/min.* The machine was capable of generating reliable load-deflection data. The specimens were simply supported at the ends leaving an overhang of about 20 *mm* at each end. The concentrated two point line load was applied at the one third spans. The complete test set up along with the data logging system is shown in Fig. 7.4. All the panels were tested up to failure. The load data corresponding to the controlled deflections were observed. First crack load and ultimate load were also recorded.

7.7 DISCUSSION ON TEST RESULTS

The aim of the present investigation was to assess the load-deflection behaviour vis-à-vis the failure characteristics of the ferrocement plate specimens. Flexural tests were undertaken on both the uninhibited and inhibited specimens. The specimens were exposed to both potable water and saline water medium. A comparison of the flexural characteristics of the inhibited plate specimens with the control specimens was done to ascertain the effectiveness of the corrosion inhibitors *viz.* calcium nitrite and tannic acid, with different inhibitor application techniques.



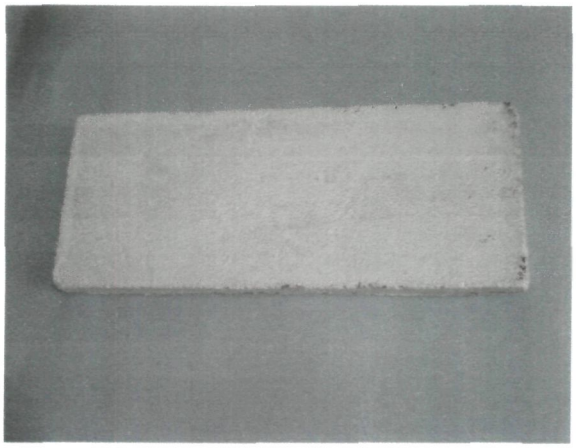
(a) Welded Wire Mesh Reinforcement



(b) Freshly Cast Plate Specimen

(c) Specimens under Wet Cycle

(d) Specimens under Dry Cycle

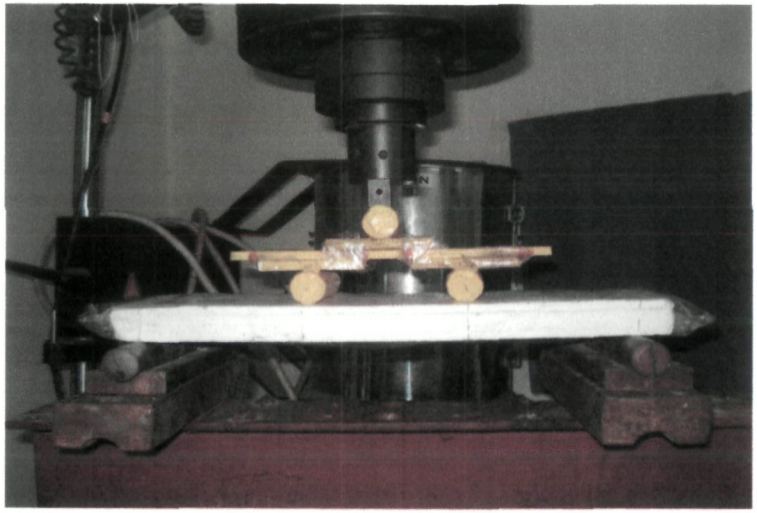


(e) White Washed Plate Specimen

(f) Set of Specimens before Test

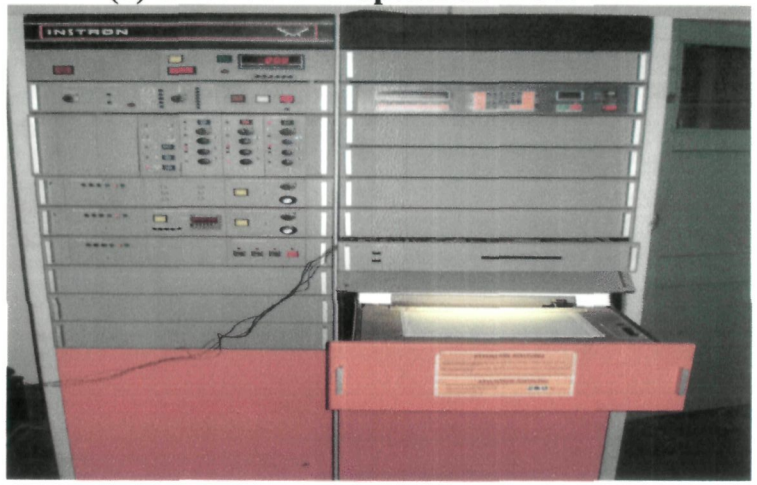
Fig. 7.3 Preparation Stages for Ferrocement Plate Specimens

(a) INSTRON UTM



(b) Close View of Specimen under Test

(c) Data Acquisition System



(d) Plotter

Fig. 7. 4 Plate Specimen under Flexural Test on INSTRON UTM

7.7.1 FERROCEMENT PLATE SPECIMENS EXPOSED TO POTABLE WATER MEDIUM

The percentage variation of the first crack load, ultimate load, deflection at first crack load and ultimate load for the inhibited specimens with respect to the control specimen, were computed and given in Table– 7.3. A comparison of the load-deflection characteristics of the uninhibited ferrocement plate control specimens (PNW) exposed to potable water medium, has been done with the load-deflection characteristics of the inhibited specimens using calcium nitrite inhibitor in two different application modes (PNW I Series and PNW SC I Series) as shown in Fig. 7.5 and Fig. 7.6, respectively. A representative plate specimen under test for PNW Series has been shown in Fig. 7.7 whereas the same for PNW I-5 series has been shown in Fig. 7.8.

Similarly, for the tannic acid inhibitor used in two different modes (PNW II-Series and PNW SC II-Series), a comparison of the load-deflection characteristics of the uninhibited ferrocement plate control specimens (PNW) with the inhibited specimens has been shown in Fig. 7.9 and Fig. 7.10.

It can be seen from the Table– 7.3 as well as the Figs. 7.5 – 7.6 and Figs. 7.9 - 7.10 that the uninhibited ferrocement plate specimens (PNW), after 360 *days* of alternate wetting and drying cycles, exhibit the lowest first crack load as well as ultimate load, as compared to all other corrosion inhibited specimens. The corrosion of the wire meshes and the subsequent loss of bond between the mortar and the wire mesh reinforcement, are primarily the main reasons behind the low load carrying capacity of these specimens. As the load was increased, both the numbers of cracks as well as the crack width were found to increase. Snapping of outer wire mesh layers was also observed resulting in sudden drop in the load carrying capacity, after which the load is subsequently taken by the inner wire mesh layers. Similar behavior has been reported by earlier investigators also (Logan and Shah, 1973; Johnston and Mowat, 1974; Balaguru, Naaman and Shah, 1977; Arif, Pankaj and Kaushik, 1999; Arif *et al.*, 2001). The absence of composite action renders the plate incapable of offering significant tensile stress resisting capacity, and as an outcome of it, de-bonding of the mortar and wire mesh layers is seen at higher loads as shown in Fig. 7.7. The cracks on the bottom surface for PNW series of specimens, as shown in the Fig. 7.11(a), further validate these observations.

Table– 7.3 Comparison of First Crack and Ultimate Load and the Associated Deflection for Ferrocement Plate Specimens Exposed in Potable Water Medium

S. No.	Specimens Designation	First Crack Load (*kN*)	% Variation in First Crack Load with respect to Control Specimen	Deflection at First Crack Load (*mm*)	Ultimate Load (*kN*)	% Variation in Ultimate Load with respect to Control Specimen	Deflection at Ultimate Load (*mm*)
1.	PNW (Control)	1.809	---	2.5	2.768	---	8.5
2.	PNW I-1	2.253	24.54	2.5	3.582	29.41	8.5
3.	PNW I-3	2.965	63.90	3.0	4.549	64.34	15.5
4.	PNW I-5	3.184	76.01	3.0	5.293	91.22	14.5
5.	PNW SC I-1	3.112	72.03	5.0	3.368	21.68	12.5
6.	PNW SC I-3	2.108	16.53	2.5	4.130	49.20	13.5
7.	PNW SC I-5	3.383	87.01	3.5	4.540	64.02	13.0
8.	PNW II-1	1.430	–20.95	1.0	2.623	–5.24	2.5
9.	PNW II-3	1.893	4.64	1.5	2.728	–1.44	3.0
10.	PNW II-5	2.757	52.40	3.0	2.927	5.74	4.5
11.	PNW SC II-1	2.041	12.82	3.0	3.020	9.10	6.0
12.	PNW SC II-3	2.334	29.02	3.0	3.639	31.47	11.5
13.	PNW SC II-5	2.251	24.43	3.5	3.763	35.95	9.0

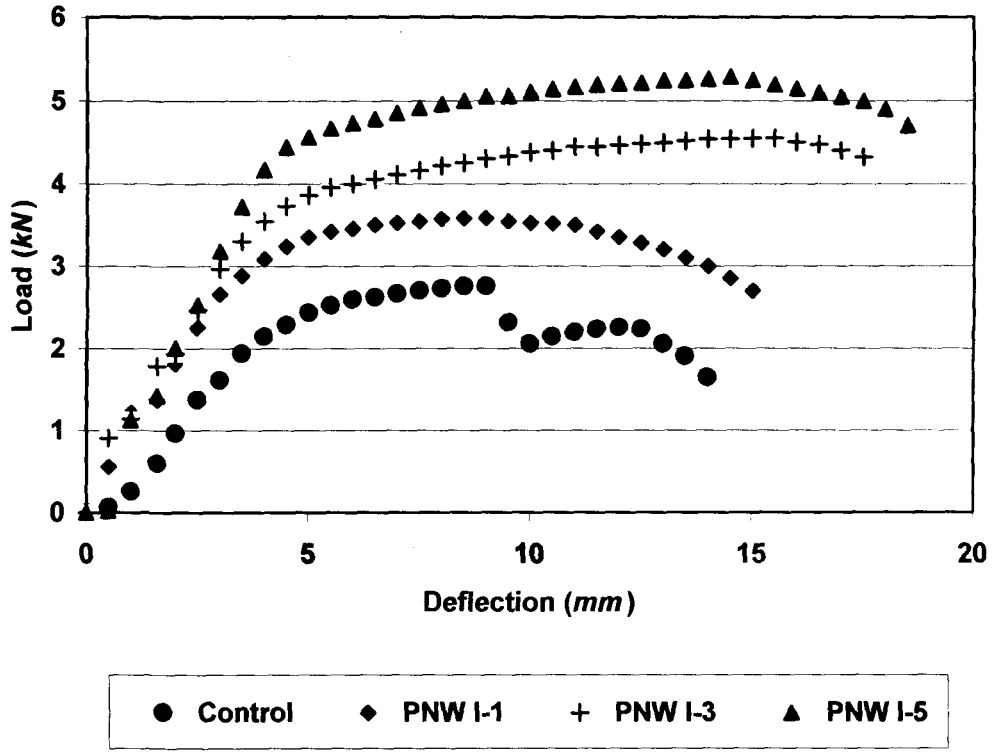


Fig. 7.5 Comparison of Load-Deflection Curve for the Ferrocement Plate Inhibited with Calcium Nitrite added in Mortar Mix (PNW I) and Exposed to Potable Water

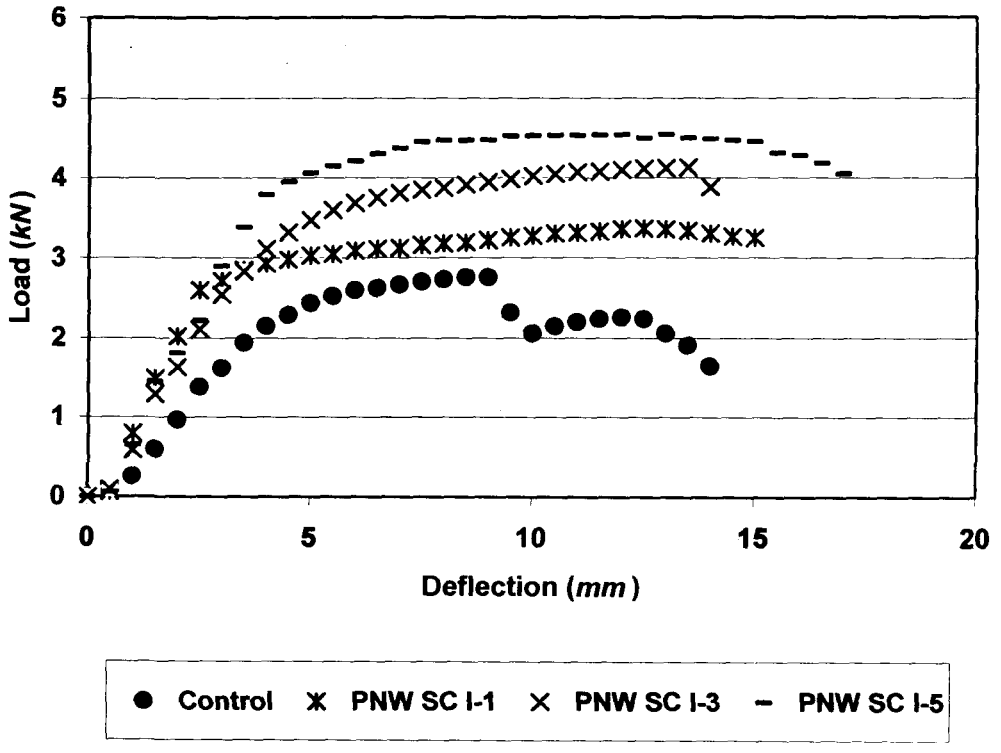


Fig. 7.6 Comparison of Load-Deflection Curve for the Ferrocement Plate Inhibited with Calcium Nitrite Used in Slurry Coated Form (PNW SC-I) and Exposed to Potable Water

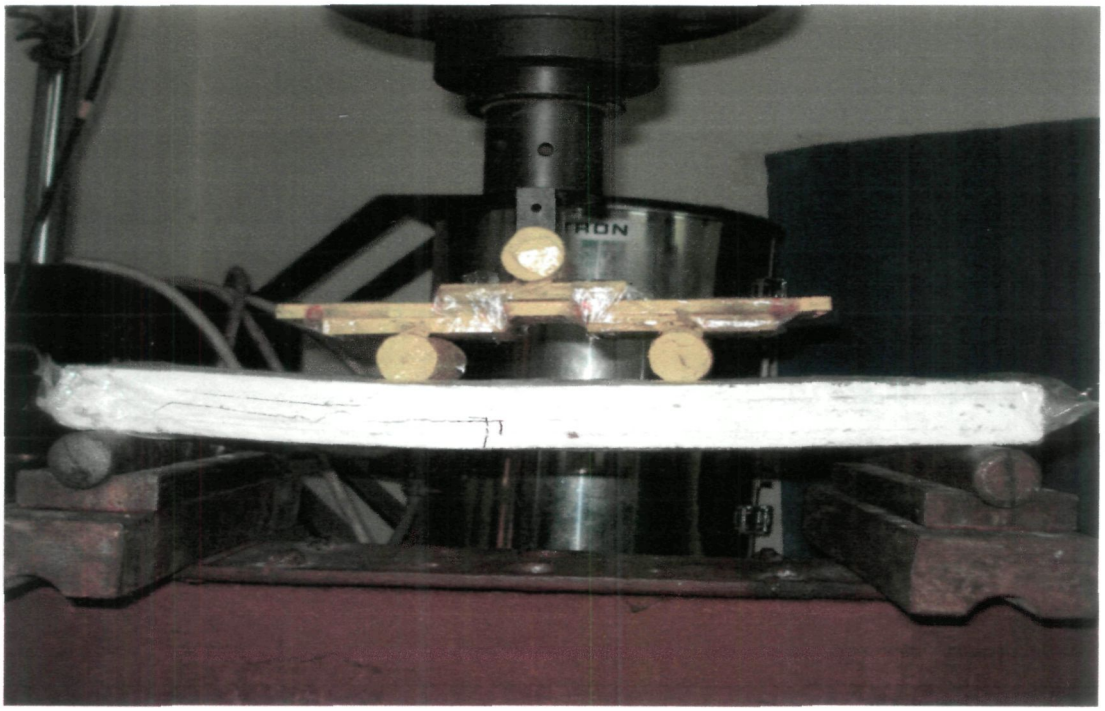


Fig. 7.7 De-bonding of Mortar Layers in Ferrocement Plate Specimen (PNW)

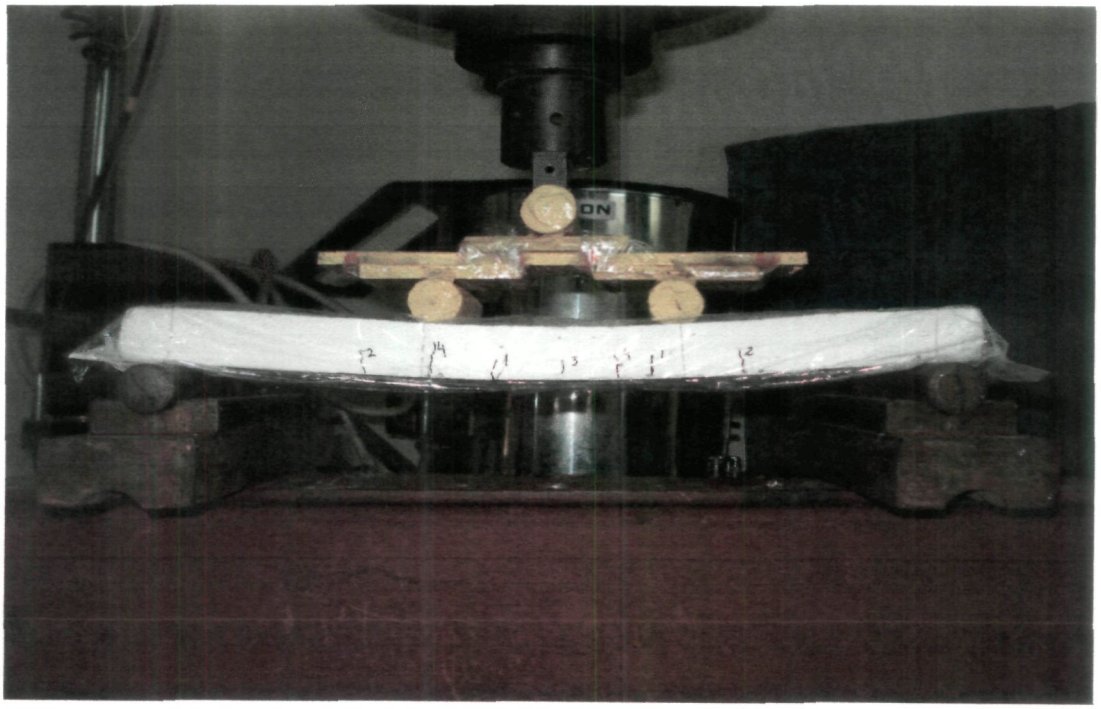


Fig. 7.8 Flexural Cracks in Ferrocement Plate Specimen with no De-bonding of Mortar Layers (PNW I-5)

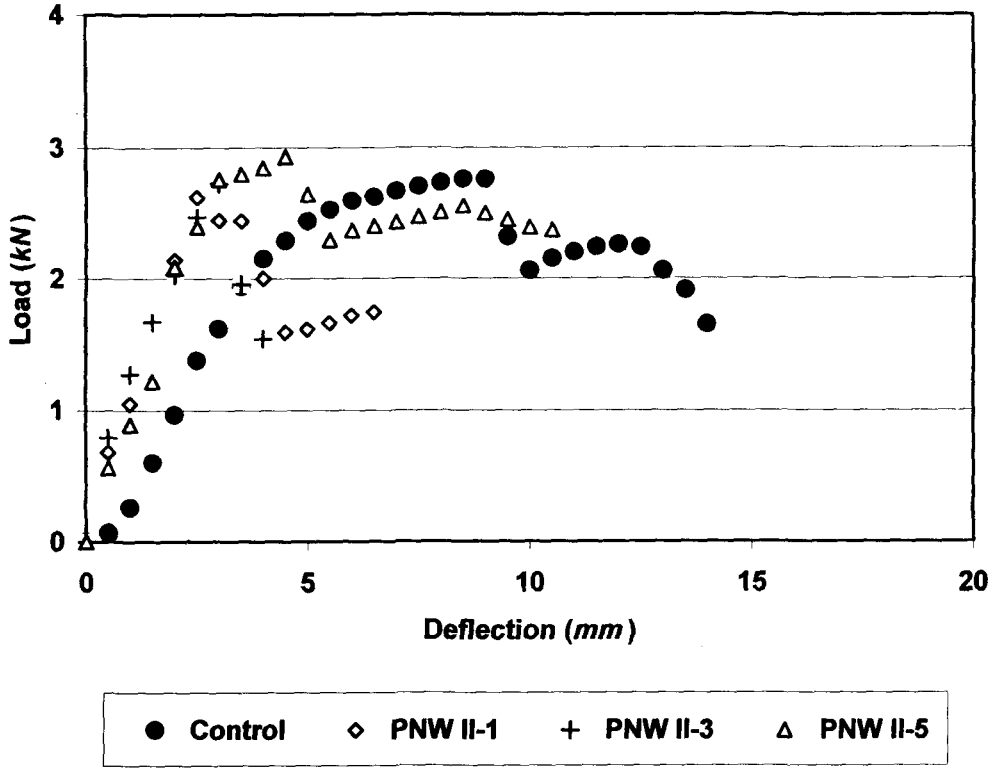


Fig. 7.9 Comparison of Load-Deflection Curve for the Ferrocement Plate Inhibited with Tannic Acid in the Form of Film over Mesh (PNW II) and Exposed to Potable Water

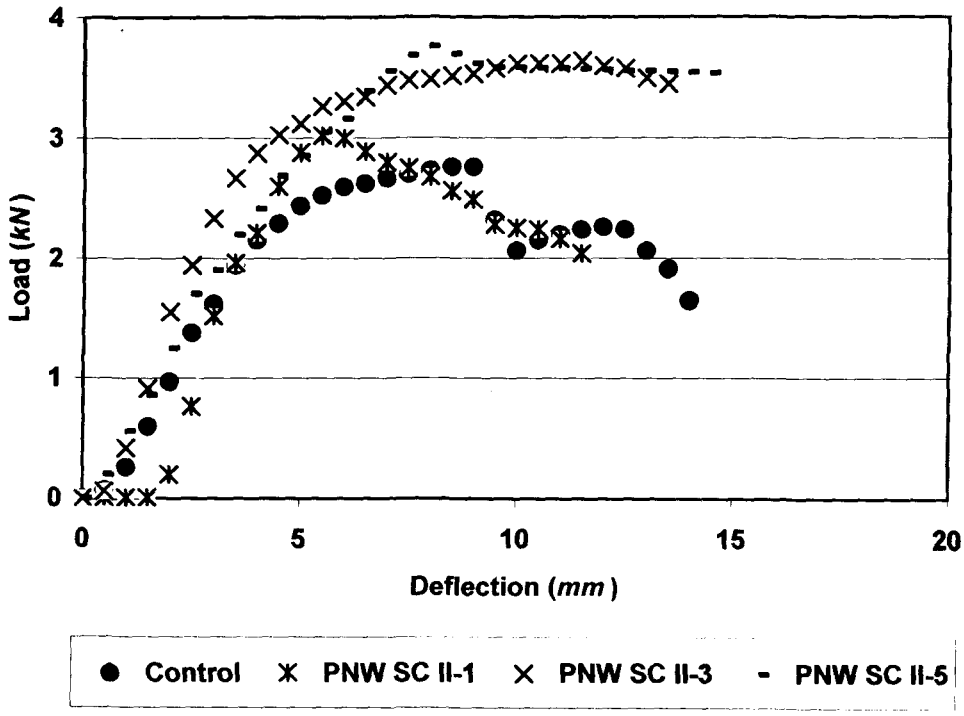


Fig. 7.10 Comparison of Load-Deflection Curve for the Ferrocement Plate Inhibited with Tannic Acid film over Mesh protected by Cement Slurry Coating (PNW SC II) and Exposed to Potable Water

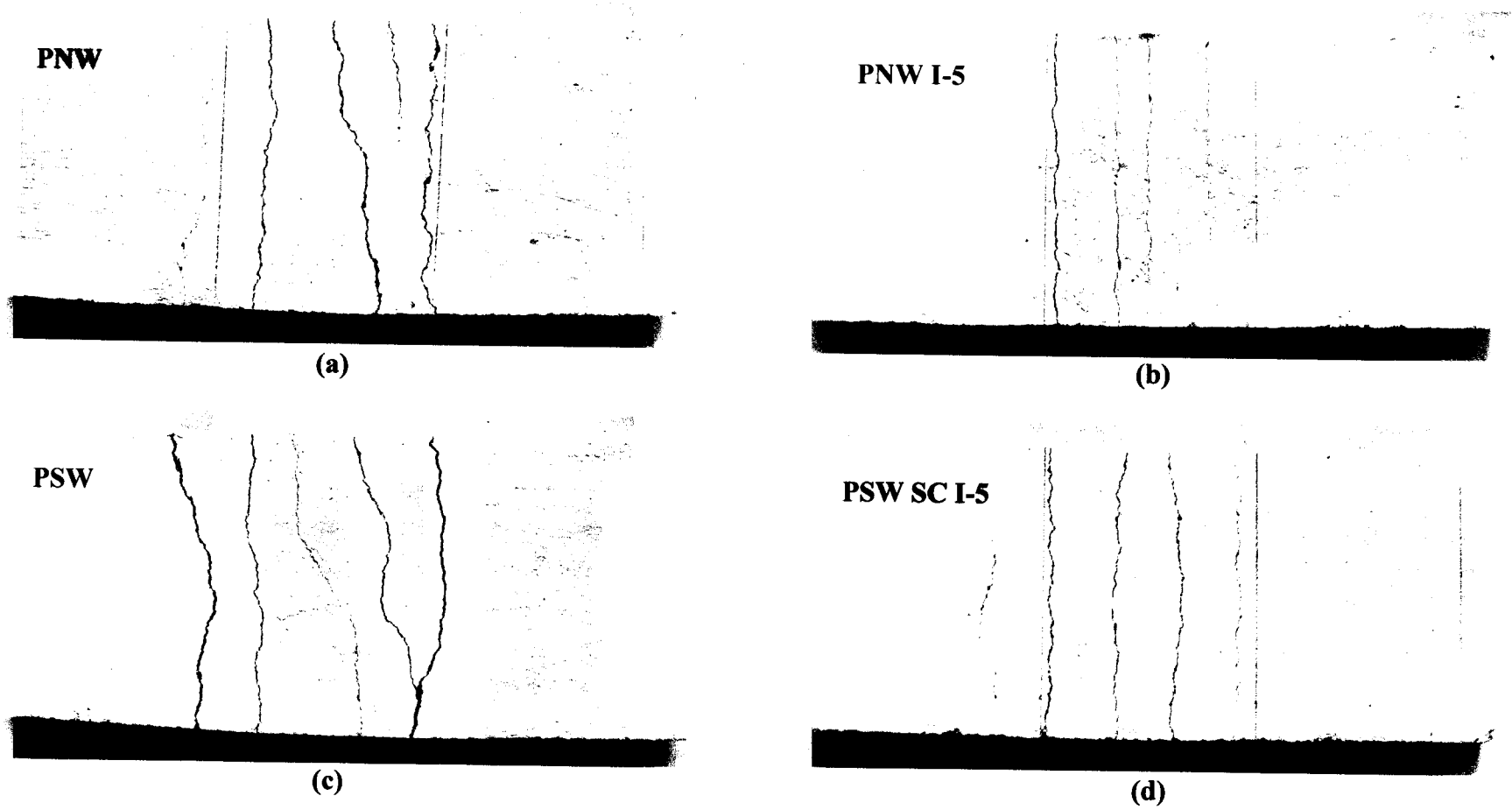


Fig. 7.11 Crack Patterns on the Bottom Surface of the Tested Ferrocement Plate Specimens

7.7.1.1 FERROCEMENT PLATE SPECIMENS INHIBITED WITH CALCIUM NITRITE IN POTABLE WATER

For the ferrocement plate specimens as stated earlier, the calcium nitrite inhibitor was used in two different ways. In the first case it was mixed directly into the cement sand mortar by weight of cement and in the second case it was mixed in cement slurry by weight of cement and the resulting paste was used to form a coating of this inhibited cement slurry over the wire mesh surface. The performance of plate specimens inhibited in these two different ways and subjected to flexural test after the completion of exposure duration, has been discussed separately as under.

CALCIUM NITRITE MIXED IN MORTAR (PNW I SERIES)

The load deflection behaviour of the specimens inhibited with calcium nitrite mixed in mortar (PNW I-Series) exposed to potable water medium, has been shown in the Fig. 7.5. A comparison of the first crack load, ultimate load and the corresponding deflection with the control specimen (PNW) has also been made and given in Table– 7.3. It is important to note here that all the inhibited specimen of this category have shown higher first crack and the ultimate load as compared to the control specimen. The increase in first crack load has been found to be 24.54%, 63.90% and 76.01% respectively for the specimens inhibited with 1%, 3% and 5% dose of calcium nitrite. The corresponding values of the ultimate strength have been observed to be higher by 29.41%, 64.34% and 91.22% respectively, as compared to the ultimate strength of the control specimen. The deflection at first crack load and ultimate load has been found to be higher for the specimen inhibited with the 3% and 5% calcium nitrite. For the specimen having 1% calcium nitrite same deflection as that of the control specimen has been observed.

The most significant reason behind the increase in flexural strength, in the specimen having inhibited mortar, is the increase in the mortar strength due to the addition of inhibitor as already reported in Chapter– 4; and also an equally effective corrosion control of wire mesh reinforcement.

The effectiveness of the calcium nitrite in controlling the corrosion in wire mesh has already been established in the Chapter–5 as well as Chapter–6. Further, since the wire meshes do not corrode, the bond between the mortar and the reinforcement remains intact, thereby; the load carrying capacity of the composite section remains intact.

This results in not only a higher a load carrying capacity with an extended deflection range but also demonstrates a ductile failure pattern. The typical flexural cracks for the specimens of PNW I-5 series can be clearly seen in Fig. 7.8. These cracks can further be seen at the bottom of the specimens as shown in Fig. 7.11(b). It is worth mention here that the mortar layers exhibit no signs of splitting and continue to be attached to the wire mesh layers indicating a perfect bond between the two phases of the composite and thus facilitating smooth and uniform transfer of the load throughout the composite section. Absolutely no signs of disintegration of mortar and wire mesh layers were observed even at the ultimate load.

CALCIUM NITRITE IN SLURRY COATED FORM (PNW SC I-SERIES)

The load deflection behaviour of the specimens inhibited with calcium nitrite applied in slurry coated form over the surface of the wire mesh (PNW SC I-Series) exposed to potable water medium, has been shown in the Fig. 7.6. A comparison of the first crack load, ultimate load and the corresponding deflection with the control specimen (PNW) has also been made and given in Table– 7.3. It is important to note here that all the inhibited specimen of this category have shown higher first crack and the ultimate load as compared to the control specimen. The increase in first crack load has been found to be 72.03%, 16.53% and 87.01% respectively for the specimens inhibited with 1%, 3% and 5% dose of calcium nitrite. The corresponding values of the ultimate strength have been observed to be higher by 21.68%, 49.20% and 64.02% respectively as compared to the ultimate strength of the control specimen. All the specimens of this series have shown higher deflection at first crack and ultimate load indicating improved ductility. The specimens of this category failed without splitting or de-bonding of layers exhibiting proper bond till the time of failure.

It is evident here that the inhibitors provide excellent passivation to the wire mesh reinforcement thereby, maintaining the load carrying capacity of the composite, even after sustained duration of exposure. Further, the corrosion free surface continues to maintain a very good bond with the matrix which is also partly strengthened by the rough surface of the wire mesh reinforcement due to the cement slurry coating and ultimately resulting in an improved in flexural behaviour of the plate specimens.

7.7.1.2 FERROCEMENT PLATE SPECIMENS INHIBITED WITH TANNIC ACID IN POTABLE WATER

Tannic acid inhibitor was also used in two ways. In the first case, coating of tannic acid was directly formed as a thin film over the wire mesh. In the second mode of application a protective coating of plain cement slurry was applied over the film of tannic acid. The performance of the two types of specimens subjected to flexural test after the completion of exposure duration has been discussed separately as under.

TANNIC ACID COATING (PNW II-SERIES)

A comparison of the first crack load, ultimate load and the corresponding deflection with the control specimen PNW has been given in Table– 7.3. The load deflection behaviour of the specimens inhibited with tannic acid in the form of coating over the surface of the wire mesh has been shown in Fig. 7.9.

It has been found that for the specimens inhibited with 1% tannic acid, the first crack load is lower by 20.95% as compared to the control specimen. For the specimen having 3% and 5% dose of tannic acid, the first crack load increases by 4.64% and 52.40% respectively as compared to the control specimen. A reduction of 5.24% and 1.44% has been observed in the ultimate strength for the specimen inhibited with the 1% and 3% dose. However, a marginal increase of 5.74% has been found as the dose of the inhibitor is increased to 5%. The deflection at first crack and the ultimate load have been observed to be on the lower side as compared to the control specimen in majority of specimens of this category thus indicating reduction in ductility.

The reason behind reduction in the load carrying capacity of the specimens inhibited with the 1% and 3% tannic acid seems to be dissolution of the tannic acid coating as the period of exposure increases. As the tannic acid coating gets depleted, corrosion in wire mesh layer is evident. Hence a reduction in the effective cross sectional area of the reinforcement coupled with the loss of bond between matrix and the reinforcement, leads to the loss of flexural strength as well as ductility in specimens.

At 5% dose, since the coating of the tannic acid is slightly thick, it appears that even after the dissolution of the tannic film; some protection has been provided leading to a marginal increase in the flexural strength. The failure pattern of the specimens of this category, go in line with the above mentioned findings.

TANNIC ACID COATING PROTECTED WITH CEMENT SLURRY (PNW SC II-SERIES)

For the specimens with wire mesh having a protective coating of plain cement slurry applied over the film of tannic acid, a comparison of the first crack load, ultimate load and the corresponding deflection with the control specimens is given in Tables– 7.3. The load deflection behaviour of these specimens is shown in Fig. 7.10. An increase in the first crack load and ultimate load has been observed for the specimen of this category. At 1%, 3% and 5% dose, the first crack load increases by 12.82%, 29.02% and 24.43% respectively as compared to control specimen. The corresponding increase in the ultimate load has been observed to be 9.10%, 31.47% and 35.95%. The inhibited specimens of this category indicate sufficient ductility.

Similar to the observations made in the previous Chapter, the tannic acid inhibitor used in this application mode improves the corrosion resistance of the specimens. The apparent reason behind the phenomenon may be attributed to the proper protection of the tannic acid passive film by the cement slurry. The increased flexural strength is very well an indication of the effective corrosion control. As the wire mesh is in passive state the bond between the wire mesh and the reinforcement remains intact. Further, the specimens of this category did not show any signs of de-lamination in contrast to what was observed for most of the specimen of PNW II group. This thus establishes the effectiveness of the application methodology for the tannic acid inhibitor in controlling corrosion.

7.7.2 FERROCEMENT PLATE SPECIMENS EXPOSED TO SALINE WATER MEDIUM

The ferrocement plate specimens were exposed to saline water medium to explore its performance when subjected to artificially simulated aggressive environment. For the purpose, the specimens were exposed to 4% *NaCl* solution. The two inhibitors used for potable water medium earlier *viz.* calcium nitrite and tannic acid, were used for saline water medium also. The same application methodologies, as used for potable water medium, were also adopted for specimens exposed to saline water medium. The flexural performance of the inhibited specimens was compared with the un-inhibited specimen exposed to saline water medium (PSW). The percentage variation of the first crack load, ultimate load, deflection at first crack load and ultimate load for the inhibited specimens with respect to the control specimen (PSW), were computed and given in Table– 7.4. A comparison of the load-deflection characteristics of the uninhibited ferrocement plate control specimens (PSW) exposed to saline water medium, has been done with the load-deflection characteristics of the inhibited specimens using calcium nitrite inhibitor in two different application modes (PSW I Series and PSW SC I-Series) as shown in Fig. 7.12 and Fig. 7.13 respectively. A representative plate specimen under test for PSW Series has been shown in Fig. 7.14 whereas the same for PSW SC I-5 Series has been shown in Fig. 7.15.

Similarly, for the tannic acid inhibitor used in two different modes (PSW II-Series and PSW SC II-Series), a comparison of the load-deflection characteristics of the uninhibited ferrocement plate control specimens (PSW) with the inhibited specimens has been shown in Fig. 7.16 and Fig. 7.17.

It can be seen from the Table– 7.4 as well as the Figs. 7.12 – 7.13 and Figs. 7.16 -7.17 that the uninhibited ferrocement plate specimens (PSW), after 360 *days* of alternate wetting and drying cycles, exhibit the lowest first crack load as well as ultimate load, as compared to all other corrosion inhibited specimens in saline water medium as well as potable water medium. The most severe corrosion of the wire meshes and the subsequent loss of bond between the mortar and the wire mesh reinforcement, are primarily the main reasons behind such a low load carrying capacity of these specimens which subsequently results in the loss of ductility also.

Table– 7.4 Comparison of First Crack and Ultimate Load and the Associated Deflection for Ferrocement Plate Specimens Exposed in Saline Water Medium

S. No.	Specimens Designation	First Crack Load (*kN*)	% Variation in First Crack Load with respect to Control Specimen	Deflection at First Crack Load (*mm*)	Ultimate Load (*kN*)	% Variation in Ultimate Load with respect to Control Specimen	Deflection at Ultimate Load (*mm*)
1.	PSW (Control)	1.250	---	2.0	1.797	---	5.0
2.	PSW I-1	1.561	24.88	3.0	1.649	-8.24	4.0
3.	PSW I-3	1.823	45.84	2.0	4.317	140.23	11.5
4.	PSW I-5	3.098	147.84	3.5	4.511	151.03	15.0
5.	PSW SC I-1	1.787	42.96	2.0	2.245	19.95	3.0
6.	PSW SC I-3	2.287	82.96	3.0	4.120	129.27	9.5
7.	PSW SC I-5	1.997	59.76	3.0	4.189	133.11	13.0
8.	PSW II-1	1.617	29.36	2.5	2.018	12.30	8.5
9.	PSW II-3	1.466	17.28	2.5	2.333	29.83	10.0
10.	PSW II-5	1.886	50.88	2.5	3.921	118.20	9.0
11.	PSW SC II-1	2.747	119.76	3.0	3.571	98.72	7.5
12.	PSW SC II-3	2.331	86.48	3.5	3.624	101.67	8.0
13.	PSW SC II-5	1.961	56.88	3.0	3.780	110.35	13.0

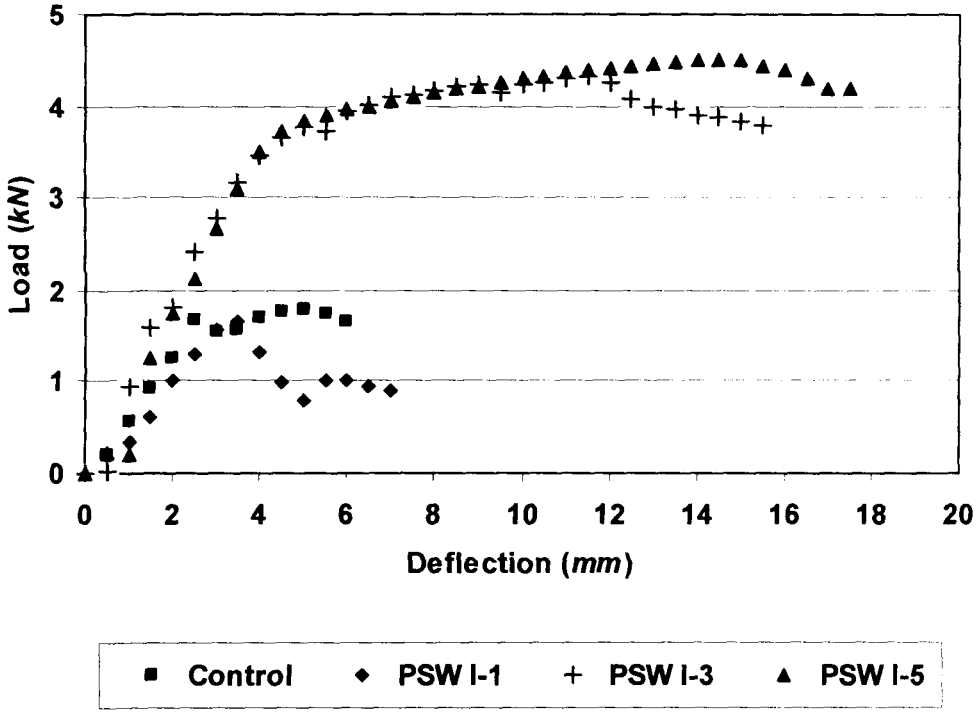


Fig. 7.12 Comparison of Load-Deflection Curve for the Ferrocement Plate Inhibited with Calcium Nitrite added in Mortar Mix (PSW I) and Exposed to Saline Water

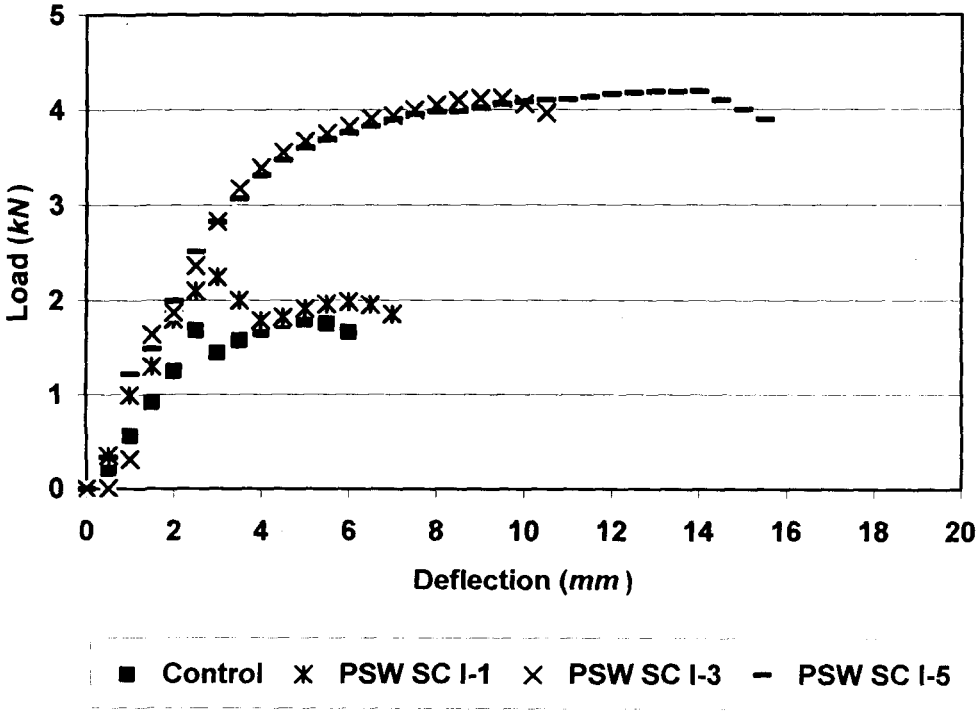


Fig. 7.13 Comparison of Load-Deflection Curve for the Ferrocement Plate Inhibited with Calcium Nitrite Used in Slurry Coated Form (PSW SC I) and Exposed to Saline Water

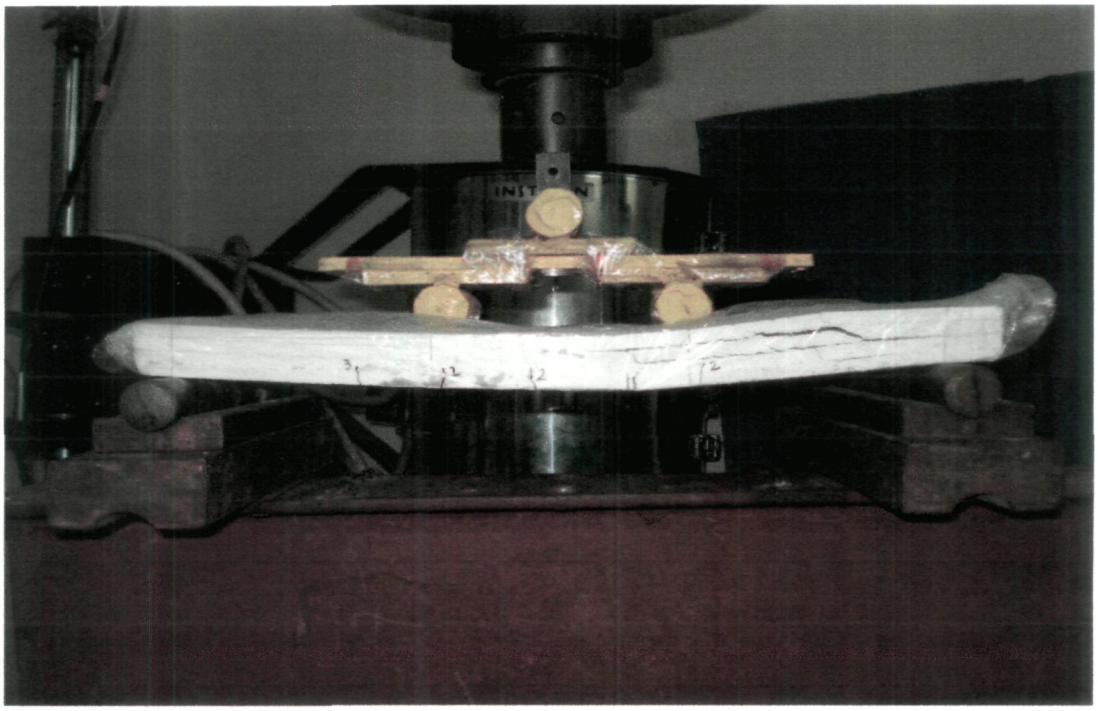


Fig. 7.14 De-bonding of Mortar Layers in Ferrocement Plate Specimen (PSW)

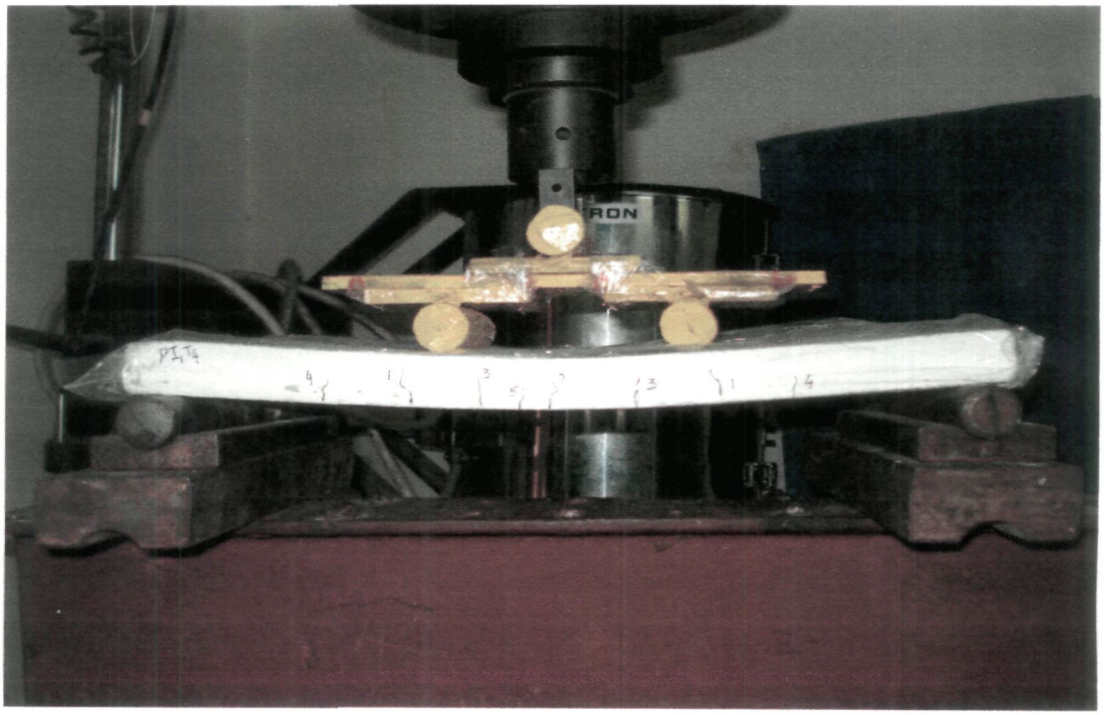


Fig. 7.15 Flexural Cracks in Ferrocement Plate Specimen with no De-bonding of Mortar Layers (PSW SC I-5)

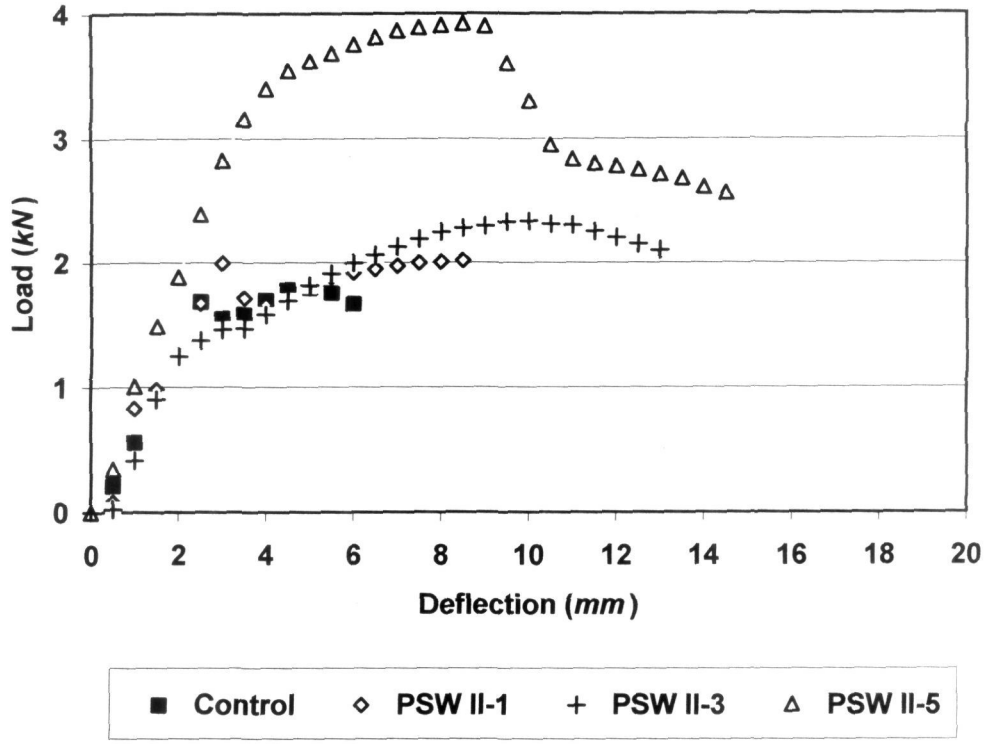


Fig. 7.16 Comparison of Load-Deflection Curve for the Ferrocement Plate Inhibited with Tannic Acid in the Form of Film over Mesh (PSW II) and Exposed to Saline Water

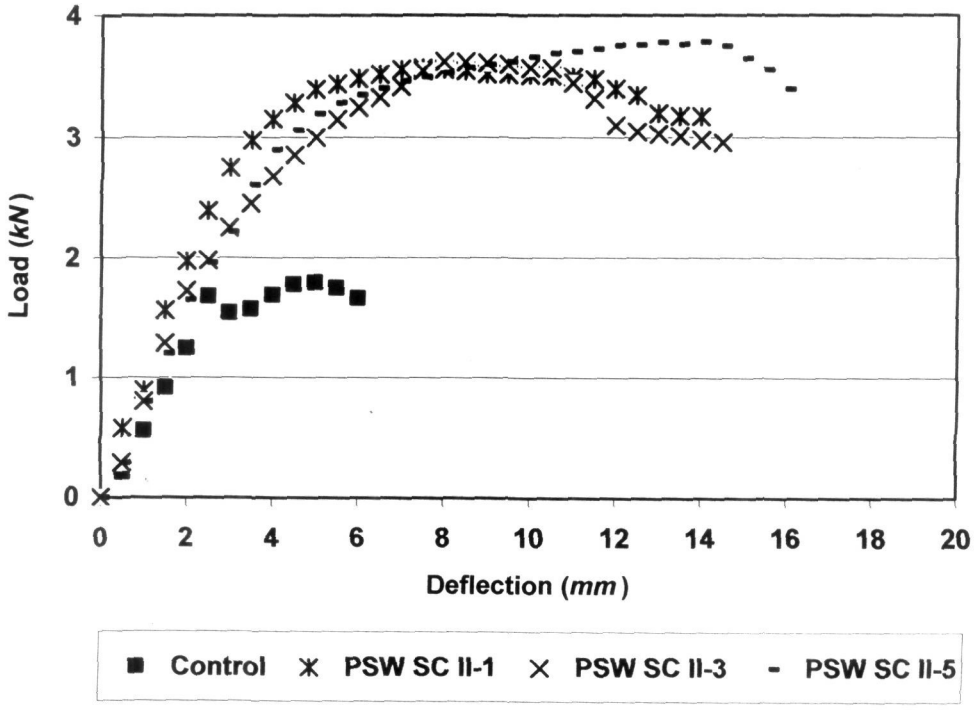


Fig. 7.17 Comparison of Load-Deflection Curve for the Ferrocement Plate Inhibited with Tannic Acid film over Mesh protected by Cement Slurry Coating (PSW SC II) and Exposed to Saline Water

As the load was increased, both the numbers of cracks as well as the crack width were found to increase. Snapping of outer wire mesh layers was also observed resulting in sudden drop in the load carrying capacity, after which the load is subsequently undertaken by the inner wire mesh layers. The failure of the specimen takes place at low strain values and thus rendering it to behave like a brittle system. Experimental tests undertaken by the earlier investigators on ferrocement plate specimens subjected to aggressive environment further validate the observed behavior (Masood *et al.*, 2003). The significant drop in the tensile stress resisting capacity, results in the de-bonding of the mortar and wire mesh layers at higher loads as shown in Fig. 7.14. The cracks on the bottom surface for PSW series of specimens as shown in the Fig. 7.11(c) further validate these observations.

7.7.2.1 FERROCEMENT PLATE SPECIMENS INHIBITED WITH CALCIUM NITRITE IN SALINE WATER

For the specimens exposed to saline water medium, the calcium nitrite inhibitor was used in the same two ways as already presented for specimen exposed to potable water medium in Section 7.7.1.1. The performance of plate specimens inhibited in these two different ways and subjected to flexural test after the completion of exposure duration, has been discussed separately as under.

CALCIUM NITRITE MIXED IN MORTAR (PSW I-SERIES)

A comparison of the first crack load, ultimate load and the corresponding deflection with the control specimens (PSW) has been made and given in Table– 7.4. The load deflection behaviour of the specimen inhibited with calcium nitrite mixed in mortar has been shown in the Fig. 7.12.

As compared to control specimen (PSW), the first crack load of the inhibited specimens of this category increases by 24.88%, 45.84% and 147.84% respectively for 1%, 3% and 5% dose of calcium nitrite. The ultimate load for 1% dose reduces by 8.24%. However, as the dose of the calcium nitrite is increased to 3% and 5% the corresponding increase in the ultimate load has been observed to be 140.23% and 151.03% as compared to control specimen.

The load deflection behaviour indicates that except for the specimen having 1% dose of calcium nitrite, the ductility of all the specimens is much higher than the control specimen. A very effective corrosion control of wire mesh reinforcement is the main reason for this excellent behaviour. Further, since the wire meshes do not corrode. the bond between the mortar and the reinforcement remains intact, thereby; the load carrying capacity of the composite section remains intact. This results in not only a higher a load carrying capacity with an extended deflection range but also demonstrates a ductile failure pattern with the plate imparting a real composite action to withstand the flexural tensile stresses. The typical flexural cracks for the specimens of PSW I-5 series can be clearly seen in Fig. 7.15. It is worth mention here that the mortar layers absolutely show no signs of splitting and continue to be with the wire mesh layers indicating a perfect bond between the two phases of the composite and thus facilitating smooth and uniform transfer of the load throughout the composite section even at higher loads. Even at the ultimate load, no signs of disintegration of mortar and wire mesh layers were observed.

The reduction in load carrying capacity at 1% dose and appreciable increase in load carrying capacity at 3% and 5% dose can be attributed to the Cl^-/NO_2^- ratio. Lower dose of the calcium nitrite results in higher Cl^-/NO_2^- ratio and hence there is every possibility of accelerated pitting of steel reinforcement in presence of chloride when insufficient nitrite ("Under dosage") is present (Dhouibi, Triki and Raharinaivo, 1999). Hence it can be concluded that at 1% dose, higher value of Cl^-/NO_2^- results in pitting corrosion, thereby, reducing the effective cross sectional area of the steel. Due to the corrosion of the reinforcement the bond between mortar and wire mesh also deteriorates. These two factors are mainly responsible for the reduction in strength and ductility. With increase in the dose of the inhibitor the effect appears to cease since the Cl^-/NO_2^- ratio improves resulting in a sharp increase in flexural strength and the ductility.

CALCIUM NITRITE IN SLURRY COATED FORM (PSW SC I-SERIES)

A comparison of the first crack load, ultimate load and the corresponding deflection with the control specimens is given in Tables– 7.4. The load deflection behaviour of the specimens inhibited with calcium nitrite applied in slurry coated form over the surface of the wire mesh has been shown in Fig. 7. 13.

For the specimen with wire mesh reinforcement having coating of inhibited cement slurry, an increase of 42.96%, 82.96% and 59.76% respectively in the first crack load has been observed for 1%, 3% and 5% dose, as compared to the control specimen (PSW). The increase in ultimate load for the corresponding doses has been observed to be 19.95%, 129.27% and 133.11%. The load-deflection curve clearly indicates an increased ductility for the specimens inhibited with 3% and 5% dose. Specimens having 1% dose have shown lower value of deflection at ultimate load as compared to control specimen.

The typical flexural cracks for the specimens of PSW SC I-5 series can be clearly seen in Fig. 7.15. These cracks can further be seen at the bottom of the specimens as shown in Fig. 7.11(d). It is clear from these figures that the mortar layers exhibit no signs of splitting and continue to be attached to the wire mesh layers indicating a perfect bond between the two phases of the composite and thus facilitating smooth and uniform transfer of the load throughout the composite section. Absolutely no signs of disintegration of mortar and wire mesh layers were observed even at the ultimate load.

The main reason behind this excellent behavior at 3% and 5% dose of inhibitor is the fact that the reinforcement is in close contact with the inhibitors that too in high concentration which perhaps provides the reasonably good corrosion inhibition. The foremost advantage of applying calcium nitrite in slurry coated form is that it nether affects the setting time of the cement nor influences the chemical reactions which take place during the process of hydration and hardening. Another advantage is the cost effectiveness of this method of application. Since only the inhibited cement slurry has to be used to form the coating over the surface of reinforcement, a very little amount of inhibitor is required. Further, a very small amount of slurry can form the inhibited coating over the surface of reinforcement required to cast a specimen.

7.7.2.2 FERROCEMENT PLATE SPECIMENS INHIBITED WITH TANNIC ACID IN SALINE WATER

For the specimens exposed to saline water medium, the tannic acid inhibitor was used in the same two ways as already presented for specimen exposed to potable water medium in Section 7.7.1.2.

A comparison of flexural characteristics of the uninhibited plate specimen with the inhibited specimens in saline water medium was undertaken. The performance of plate specimens inhibited in these two different ways and subjected to flexural test after the completion of exposure duration, has been discussed separately as under.

TANNIC ACID COATING (PSW II-SERIES)

A comparison of the first crack load, ultimate load and the corresponding deflection with the control specimens is presented in Table– 7.4. The load deflection behaviour of the specimen inhibited with calcium nitrite mixed in mortar is given in the Fig. 7.16.

For the ferrocement plate specimens inhibited with the 1%, 3% and 5% dose of the tannic acid, the first crack load is observed to increase by 29.36%, 17.28% and 50.88% respectively, as compared to the control specimen (PSW). The corresponding increase in the ultimate load has been found to be 12.30%, 29.83% and 118.20%. The values of deflection at first crack and ultimate load also indicate an extended deflection range thus resulting in an appreciable increase in the ductility of the specimens of this category.

For the specimen with 5% dose of tannic acid (PSW II-5), the corrosion inhibitor have been found to be very effective thus an increased load carrying capacity with a consistent composite performance of the plate has been observed. However, in a few specimens de-bonding of wire mesh layers with the mortar layers has also been observed resulting in a horizontal split. As a whole, it appears that the level of inhibition provided by the passivating film of tannic acid is far more effective in these specimens as compared to the specimens of the same category (PNW II-Series), exposed in potable water medium.

TANNIC ACID COATING PROTECTED WITH CEMENT SLURRY (PSW SC II-SERIES)

The flexural behaviour of the specimen inhibited with tannic acid coating protected by plain cement slurry applied over the surface of the wire mesh and exposed to saline water medium was also investigated. The load deflection behaviour of these specimens (PSW SC II-Series) is given in the Fig. 7.17. A comparison of the first crack load, ultimate load and the corresponding deflection with the control specimens is given in Tables– 7.4.

An increase of 119.76%, 86.48% and 56.88% respectively, in the first crack load and 98%, 101.67% and 110.35% respectively, in ultimate load has been observed for the specimens inhibited with the 1%, 3% and 5% dose, as compared to the control specimen (PSW). Appreciable increase in the deflection at first crack load and ultimate load has been observed for the specimen of this category.

The increased flexural strength indicates an effective corrosion control. Since the coating of the tannic acid is very well protected by the cement slurry coating, the wire meshes are found to be in passive state. An improved bond between the wire mesh and the reinforcement is also observed as the specimens fail without any splitting or de-bonding. The cracks in most of these specimens have been observed to be in the middle third zone of the plate indicating a proper composite action facilitating a smooth transfer of the load.

7.8 CONCLUDING REMARKS

A pronounced corrosion activity, resulting in a considerable loss in flexural strength, is observed in un-inhibited ferrocement plate specimens exposed to potable water medium (PNW) as well as saline water medium (PSW). The failure is mainly on account of de-bonding of wire mesh layers with the mortar layers. A far more severe corrosion is observed in PSW series of specimens. The corrosion of the wire meshes and the subsequent loss of bond between the mortar and the wire mesh reinforcement, results in a low load carrying capacity of these specimens. As the loads are increased, both the numbers of cracks as well as the crack width increase. The failure of the PSW series of specimens, takes place at low strain values and thus rendering it to behave like a brittle system. The cracks on the bottom surface for PNW and PSW series of specimens further validate these observations.

Among the inhibited ferrocement plate specimens exposed to potable water medium, best results have been obtained for the calcium nitrite inhibited specimens. For both the two application methodologies, *i.e.* when it is used in mix (PNW I-Series) or when it is used in slurry coated form (PNW SC I), an increase in the first crack load and the ultimate load has been observed.

Highest increase in flexural strength was obtained for the specimen inhibited with 5% calcium nitrite, mixed with mortar. The reason behind almost two fold increase appears to be the protection provided by the calcium nitrite to the wire mesh reinforcement thereby providing a perfect bond between mortar and the wire meshes. The other reason may be cited here is the fact that the mortar strength increases due to higher percentage of the calcium nitrite, hence improving the composite strength as a whole. Even at 3% dose quite high value of first crack load and ultimate load have been observed.

The specimens with cement slurry protection over tannic acid coating (PNW SC II) have shown appreciable increase especially at 3% and 5% inhibitor dose. However, in the specimens where no such protection (PNW II) has been provided to the tannic acid coating, only a marginal increase in the strength is observed. The failure mode of these specimens also supplements these findings.

The observations made during the flexural tests and also the load-deflection behaviour of the specimens, clearly indicate that the specimen failed through de-lamination of the mortar layers, indicating loss of bond between the mortar and the reinforcement due to corrosion.

In saline water medium, the ferrocement plate specimens inhibited with the calcium nitrite, have shown a higher flexural strength for 3% and 5% dose of inhibitor, in both the two application schemes, whether calcium nitrite was mixed in mortar (PSW I) or used in slurry coated form (PSW SC I). However at 1% dose of calcium nitrite mixed in mortar, a value lower than the control specimen was observed. For the specimens where the reinforcement was coated with 1% calcium nitrite in the form of inhibited cement slurry, only a marginal increase in ultimate load carrying capacity has been observed. The reason behind the calcium nitrite not being so effective in mitigating corrosion at 1% dose in saline water exposure medium appears to be the higher value of Cl^-/NO_2^- ratio. The failure is triggered by de-bonding of wire mesh layers with the mortar layers. An excessive corrosion activity appears to be the reason behind this.

In tannic acid inhibited specimens (PSW II) exposed in saline water medium, only at higher dose of 5%, the inhibition efficiency similar to the specimens inhibited with calcium nitrite has been observed. At lower doses, only a marginal increase in the value of flexural strength has been found. The reason behind the effectiveness of 5% dose of inhibitors appears to be a thick coating of the tannic acid that remains effective even after it gets dissolved with the passage of time. However, for the specimens having reinforcement inhibited with tannic acid film protected with the cement slurry (PSW SC II), the flexural strength almost double than that for the control specimen has been observed. The failure characteristic of these specimens is very much similar to that of their counterpart specimens inhibited with calcium nitrite wherein the clear composite action is exhibited indicating a perfect bond between the wire mesh reinforcement and the mortar.

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Chapter 8

Conclusions and Scope for Further Study

8.1 CONCLUSIONS

With the aim to prevent the corrosion in the ferrocement composites using corrosion inhibitors and thereby improving the durability of the ferrocement composites, detailed experimental investigations were undertaken. In the first part of the study, an attempt was made to assess the suitability of using some organic and inorganic corrosion inhibitors for cementitious composites like ferrocement. On the basis of their performance and the desired physical and chemical properties, two inhibitors were finally selected for further investigations on naked mild steel plate, naked welded steel wire mesh and cement slurry coated welded steel wire mesh specimens with varying dose of inhibitors as well as exposure duration for both potable and saline water exposure medium. The suitability and effectiveness of these corrosion inhibitors was further investigated for ferrocement cuboid specimens containing three layers of wire meshes when exposed to normal and aggressive environment. Both quantitative and qualitative assessments were made. Experimental investigations were finally undertaken on scaled ferrocement plate specimens using these inhibitors to establish their suitability for controlling and mitigating the corrosion in the ferrocement plate specimens with main focus on their load-deflection behaviour vis-à-vis failure characteristics of these specimens. Some of the significant conclusions and observations emerging from the study are presented here.

8.1.1 SELECTION OF CORROSION INHIBITORS

- It has been observed that most of the inhibitors *viz.* calcium nitrite, calcium nitrate, calcium stearate and tannic acid, acted as an accelerator to the initial and final setting of the cement, though the rate of acceleration was different in each case. However, it is interesting to note that at higher doses some of the inhibitors (5% calcium nitrite and tannic acid) behaved as retarders. However, the values of the initial and final setting time are within the recommended limits of the relevant codes of practice.
- An increase in compressive and tensile strength has been observed with age for the control, saline and most of the mortar mixes with varying dose of inhibitors.
- For some inhibitors, the early gain in strength was much lower than the control specimen especially for the inhibited specimens containing 3% and 5% dose of tannic acid and calcium stearate. Slow gain in strength at early age in some of the combinations can be attributed to the slow down of the reaction of C_3S by the addition of these chemicals in high concentration. A significant increase in strength after 28 *days* has been observed for calcium nitrate, which is perhaps due to the fact that the C_3S reaction gains momentum after 28 *days*. These chemicals might be acting as a catalyst to the C_2S reaction too, which also contributes to the gain in delayed strength.
- With calcium nitrite inhibitor, the pH value increases whereas for calcium nitrate, tannic acid and calcium stearate, there is a slight reduction in pH value. When these inhibitors are used in cement slurry solution, the pH value is generally found to be above 12.
- The SEM images for control specimens in potable water reveal a normal hydrated structure such as calcium silicate hydrate (*CSH*) gel, scattered crystallized calcium hydroxide and unfilled pores. However, for the control specimen in saline water, pores appear to be filled by sodium chloride crystals; and for the inhibited specimens, with the crystals of inhibitors. The strength variation is on account of enhanced packing and chemical reactions of the inhibitor with C_3S, C_2S and C_3A.
- The electrochemical Tafel extrapolation and AC impedance technique tests indicate a better performance for calcium nitrite inhibitor as compared to other three inhibitors. The calcium nitrate did not perform well. In some cases calcium stearate has shown better results whereas in some other conditions tannic acid performed well.
- The calcium nitrite and tannic acid inhibitors were finally chosen as the best inorganic and organic inhibitors respectively, for further studies.

8.1.2 TESTS ON MILD STEEL PLATE, NAKED AND SLURRY COATED WIRE MESH

- All the three types of specimens *viz.* mild steel plate, naked welded steel wire mesh and the cement slurry coated welded steel wire mesh specimens; undergo higher corrosion when exposed to saline water medium as compared to their counterparts exposed to potable water medium for all of the exposure durations considered.
- For the mild steel plate specimens, only 1% dose of the calcium nitrite is sufficient in controlling the corrosion throughout the exposure duration. However, in saline water medium 1% dose is effective only up to short duration of exposure; and for longer durations, a calcium nitrite dose of 3% was found to be sufficient. Tannic acid inhibitor has not been found to be very effective in controlling the corrosion, owing to the dissolution of protective coating in the aqueous solution. This phenomenon is more profound in saline water medium for longer duration of exposure.
- For naked welded steel wire mesh specimens, behavior similar to that of the mild steel plate specimens was observed. The reason behind 1% dose of calcium nitrite not being so effective in saline water medium appears to be the higher chloride to nitrite ratio. For longer durations in saline water medium however, calcium nitrite dose of just above 3% is found to be sufficient. However, at 5% dose the specimen was almost in fully passive state. The tannic acid has not been found very effective mainly in saline water medium for longer duration of exposure.
- For the cement slurry coated welded steel wire mesh specimens, the calcium nitrite dose of 3% has been found to sufficient in checking the corrosion both in potable and saline water medium. For the tannic acid, for all the doses for all exposure durations, almost similar level of protection has been observed. Even 1% dose is found to impart satisfactory performance. The enhanced pH of medium and the protection of tannic acid film by cement slurry coat help in corrosion protection.
- The corrosion free and spotless surface as evident in the high magnification microscopic images of the specimens captured at 400X, make it explicitly clear that the corrosion inhibitors play a key role in mitigating/controlling corrosion in both potable and saline water exposure medium.
- The corrosion inhibition efficiency, corrosion rate and corrosion penetration values for calcium nitrite and tannic acid inhibitors also substantiate the above findings.

8.1.3 TESTS ON FERROCEMENT CUBOIDS

- For ferrocement cuboid specimens, calcium nitrite exhibits an extremely high corrosion inhibition in potable water medium. For 3% and 5% dose of calcium nitrite in both the situations *i.e.* when it has been mixed with the mortar (NW I) and when applied in the form of inhibited cement slurry (NW SC I), a perfect passive state has been achieved even after 360 *days* of exposure. Visual inspection substantiates these observations as the wire meshes are found to be absolutely free from any sign of corrosion initiation. Even for 1% dose applied in the form of the inhibited cement slurry (NW SC I-1), similar level of inhibition has been achieved as that of the inhibition exhibited at higher doses.
- For the cuboid specimens in saline water exposure medium, 5% dose of calcium nitrite gives the absolute passive state for both the application methodologies (SW I and SW SC I). Even at 3% dose, quite high inhibition has been obtained. For the specimen having 5% dose of calcium nitrite, corrosion is fully abated.
- Within the two modes of application of calcium nitrite, the one where the inhibitor is applied in the form of inhibited cement slurry (NW SC I and SW SC I), appears to perform better since the inhibitor is present in high concentration and in close contact with the reinforcement. The advantages of applying calcium nitrite in slurry coated form is that it neither affects the setting time of the cement and nor it influences the chemical reactions which take place during the process of hydration and hardening. Another advantage is the cost effectiveness of this application technique.
- For the tannic acid inhibited cuboid specimens, best results have been obtained when the tannic acid film over the wire mesh was protected by the cement slurry coating (NW SC II and SW SC II). The effect of increase in the dose of tannic acid seems to be marginal for specimens in this category. In potable water exposure medium, the level of inhibition exhibited by all the doses is extremely high. In saline water medium, however, 3% and 5% doses have shown high inhibition. At lower dose, relatively low corrosion inhibition has been obtained. The reason behind the ineffectiveness of the tannic acid in the form of film without the protection of the cement slurry coating is its dissolution. When water percolates up to the surface of the reinforcement, it appears that the tannic acid coating dissolves with the passage of time, thus leaving a depleted protective layer. Visual examinations of these specimens also confirm the above findings.

- As the weight loss in the inner layer of wire mesh is only marginally less than the outer layer of the wire mesh, it can be fairly concluded that even a higher mortar thickness available for the inner wire meshes, provides only a little relief from corrosion. It is, therefore, pertinent here to plan out strategies for the corrosion protection of both outer and inner wire mesh layers.
- Very high durability factor has been obtained for most of the calcium nitrite inhibited specimens, which clearly indicates its effectiveness in enhancing the life of the reinforcement used in the form of meshes. Even for the tannic acid, except for a few of the combinations, reasonably high durability factor has been observed.

8.1.4 FLEXURAL TESTS ON FERROCEMENT PLATES

- A pronounced corrosion activity, resulting in a considerable loss in flexural strength, is observed in un-inhibited ferrocement plate specimens exposed to potable water medium (PNW) as well as saline water medium (PSW). The failure is mainly on account of de-bonding of wire mesh layers with the mortar layers. A far more severe corrosion is observed in PSW series of specimens. The corrosion of the wire meshes and the subsequent loss of bond between the mortar and the wire mesh reinforcement, results in a low load carrying capacity of these specimens. As the loads are increased, both the numbers of cracks as well as the crack width increase. The failure of the PSW series of specimens, takes place at low strain values and thus rendering it to behave like a brittle system. The cracks on the bottom surface for PNW and PSW series of specimens further validate these observations.
- The calcium nitrite inhibitor gives the best results for plate specimens exposed to potable water medium. For both the two application methodologies, *i.e.* when it is used in mix (PNW I Series) and when it is used in slurry coated form (PNW SC I), an increase in the first crack load and the ultimate load has been observed. Highest increase in flexural strength was obtained for the specimen inhibited with 5% calcium nitrite, mixed with mortar mainly because of the protection provided by the calcium nitrite to the wire mesh reinforcement thereby providing a perfect bond between mortar and the wire meshes. Also, the mortar strength increases due to higher percentage of the calcium nitrite, hence improving the composite strength as a whole.

- The specimens with cement slurry protection over tannic acid coating (PNW SC II), have shown appreciable increase especially at 3% and 5% inhibitor dose. However, in the specimens where no such protection (PNW II) has been provided to the tannic acid coating, only a marginal increase in the strength is observed. The observations made during the flexural tests and also the load-deflection behaviour of the specimens clearly indicate that the specimen failed through de-lamination of the mortar layers. indicating loss of bond between the mortar and the reinforcement due to corrosion.
- In saline water medium, the ferrocement plate specimens inhibited with the calcium nitrite show a higher flexural strength for 3% and 5% dose of inhibitor in both the two application schemes, whether calcium nitrite was mixed in mortar (PSW I) or used in slurry coated form (PSW SC I). The reason behind 1% dose of calcium nitrite not being so effective in mitigating corrosion appears to be the higher value of Cl^-/NO_2^- ratio. The failure is triggered by de-bonding of wire mesh layers with the mortar layers. A severe corrosion activity is the main reason behind this.
- The tannic acid inhibited specimens (PSW II) exposed to saline water medium, inhibition efficiency similar to the specimens inhibited with calcium nitrite is observed only at 5% dose. The reason behind the effectiveness of inhibitors appears to be a thick coating of the tannic acid that remains effective even after it gets dissolved with the passage of time. However, at lower doses, a marginal increase in the value of flexural strength is found.
- For specimens inhibited with tannic acid film protected with the cement slurry (PSW SC II), the flexural strength almost double than that of the control specimen has been observed. A very good bond between the wire mesh reinforcement and the mortar results in a perfect composite action leading to ductile failure.

8.2 SCOPE FOR FURTHER STUDY

Durability of ferrocement composites is a major thrust area of research. Little advancement has so far been made towards corrosion control in ferrocement using chemical inhibitors especially under aggressive environment. There is a wide scope left for both experimental and analytical investigations on these corrosion inhibitors in order to develop a better understanding and confidence for their potential use in cementitious composites.

Some of the following aspects need immediate attention:

- Investigations need to be undertaken on modified mortar mixes utilizing some pozzolanic materials with different types and geometries of wire mesh.
- The effect of variation in the salinity level and comparatively longer exposure duration on the corrosion inhibition efficiency should also be studied.
- Studies on some other types of corrosion inhibitors should be undertaken and an appropriate application methodology as well as dose must be ascertained.
- Numerical simulation of the mechanical behaviour of corrosion inhibited ferrocement composite specimens exposed to aggressive environments should be undertaken using appropriate modeling approaches.
- Statistical and stochastic approaches for the analysis of corrosion in distressed structures must be used and appropriate corrosion repair and rehabilitation strategies employing corrosion inhibitors must be propounded.